Renewable and Sustainable Energy Reviews 15 (2011) 4378–4399

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Modern heterogeneous catalysts for biodiesel production: A comprehensive review

A.P. Singh Chouhan, A.K. Sarma*

Sardar Swaran Singh National Institute for Renewable Energy, 12 Km Stone, Jalandhar-Kapurthala Road, Wadala Kalan, Kapurthala, Punjab 144601, India

ARTICLE INFO

Article history:
Received 5 April 2011
Accepted 5 July 2011
Available online 22 September 2011

Keywords:
Biodiesel
Transesterification
Heterogeneous catalyst
Basic catalyst
Acidic catalyst

ABSTRACT

Steep hikes of petroleum prices and rising demand of petroleum products compels the scientific society to think for the renewable alternative fuels like biodiesel. Biodiesel production is generally carried out through the process of transesterification reaction. The reaction is facilitated with a suitable catalyst either homogeneous or heterogeneous. The selection of appropriate catalyst depends on the amount of free fatty acids in the oil. Heterogeneous catalyst provides high activity, high selectivity, high water tolerance properties and these properties depend on the amount and strengths of active acid or basic sites. Basic catalyst can be subdivided based on the type of metal oxides and their derivatives. Similarly, acidic catalyst can be subdivided depending upon their active acidic sites. New varieties of mixed catalyst are also available in literatures. Catalyst generated from bio-waste and other biocatalysts which are heterogeneous in nature and extensively reported in literature are also reviewed. This review focused about the recent invention and use of the heterogeneous acid, base and biocatalysts for biodiesel production and their suitability for industrial application.

Contents

* Corresponding author. Tel.: +91 1822255543; fax: +91 1822255543.
E-mail address: anil_tu@yahoo.co.in (A.K. Sarma).

1364-0321/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.rser.2011.07.112

1. Introduction

At present the focus of the human society is to produce energy from low carbon sources and introduction of eco-friendly Green Technology. Biodiesel, the alternative renewable liquid fuel, derived from triglycerides holds promise to compensate the increase demand of petroleum diesel [1]. The process of transesterification of triglyceride with methanol, ethanol or any other suitable alcohol produces biodiesel [2–4].

Transesterification, also called alcoholysis, is the reaction of an oil or fat with an alcohol to form esters and glycerol. The basic reaction is depicted in Fig. 1. Transesterification consists of three consecutive reversible reactions viz.; conversion of triglyceride to diglyceride, diglyceride to mono glyceride and monoglyceride to fatty ester and glycerol [5]. The reaction is facilitated with a suitable catalyst [6]. If the catalyst remains in the same (liquid) phase to that of the reactants during transesterification, it is homogeneous catalytic transesterification. On the other hand, if the catalyst remains in different phase (i.e. solid, immiscible liquid or gaseous) to that of the reactants the process is called heterogeneous catalytic transesterification [7,8]. The heterogeneous catalytic transesterification is included under Green Technology due to the following attributes: (1) the catalyst can be recycled (reused), (2) there is no or very less amount of waste water produced during the process and (3) separation of biodiesel from glycerol is much easier [9,10]. During homogeneous catalytic transesterification the glycerol produced is of low quality and requires lengthy process and distillation for purification [11–14]. All these processing increases the cost of the end products: biodiesel and glycerin. Moreover, the homogeneous base catalyzed transesterification process encountered problems to handle multiple feed stocks. On the other hand, heterogeneous catalytic transesterification process overcomes these problems because methanol or ethanol does not mix with solid heterogeneous catalyst. After the transesterification reaction it is relatively easy to separate the catalyst from biodiesel and glycerol.

Oils (non-edible) with higher fatty acid content lead to the formation of soap, consequent loss of oil and problems of product separation during homogeneous catalytic transesterification [15,16]. The major drawback of the homogeneous catalyst (NaOH, KOH) is found for its hygroscopic nature, hazardous for the environment as compared to heterogeneous catalyst. The use of enzyme catalytic production of biodiesel has attracted much attention in recent years because enzymes tolerate free fatty acid and water contents, facilitating easy purification of biodiesel and glycerol. However, enzymatic transesterification could not be commercialized for production of biodiesel due to long residence time and high cost [17–19]. Heterogeneous catalyst converts triglycerides into biodiesel slowly but produced biodiesel in a very feasible economic way due to the reusability of catalyst for both the processes, e.g. batch and continuous [20–22].

Dossin et al. [23] demonstrated the first heterogeneous catalytic transesterification pilot plant using MgO as catalyst, triolin and methanol as feedstock with a production capacity 1,00,000 tonnes per year. An ideal solid catalyst (heterogeneous catalyst) favors the following steps such as large pore size to minimize diffusion problems [24,25]. High concentrations of acid sites, high catalytic stability against leaching and poisoning effects and the possibilities to tune the hydrophobicity of the surface to promote the preferential adsorption of substrates and repulsion of highly polar compounds which could cause deactivation [26]. On the basis of the reported literature catalysts can be generally classified into homogeneous, heterogeneous and biocatalyst [1,7–9,27–36] which are listed under in the flow chart (Fig. 2), including their subclassification. Table 1 presented below summarizes the reported work in the last 5-year and their brief inclusions in the review articles [1,7–10,29–31,33,35,37,38].

A large numbers of heterogeneous catalysts such as alkali metal oxides and derivatives [39–43], alkaline earth metal oxides and derivatives [42,44–51], transition metal oxides and derivatives [52–55], mixed metal oxides and derivatives [3,57–68], ion exchange resins type acid heterogeneous catalyst [21,69–73], sulfated oxides as a acid heterogeneous catalyst [22,70–84], carbon based heterogeneous catalysts [85–87], boron group base heterogeneous catalyst [3,57,58,60–65,67,68] waste material based heterogeneous catalysts [88–92], enzyme based heterogeneous catalyst [93–95] are found in literatures in the recent years and their uses in laboratory scale biodiesel production. All the efforts have been made to include recent literature so as to select suitable catalyst for industrial applications. The authors emphasize the catalytic activity, selectivity, catalyst loading, catalyst reusability and the summary for future prospects through classical and graphical representations.

2. Base heterogeneous catalyst

A general divalent metal oxide catalyst having substantial amount of covalent character facilitates the transesterification reaction as depicted in Fig. 3.

Some of the commonly used heterogeneous base catalyst are K/γ-Al_2O_3 catalyst [96], $HTiO_2$ hydrotalcite catalyst [97], Ca and Zn mixed oxide [98], Al_2O_3 supported CaO and MgO catalysts [3], alkaline earth metal oxides [47], KF/Ca–Al [99], basic zeolites, alkali metal loaded alumina [100]. A process flow diagram for biodiesel production using heterogeneous base catalyst has been depicted in Fig. 4.

2.1. Biodiesel production with alkaline earth metal oxides and derivatives

2.1.1. MgO as a base heterogeneous catalyst

Alkaline earth metals such as Be, Mg, Ca, Sr, Ba and Ra, their oxides and derivatives are used by different researchers. MgO and SrO are widely used among the other alkaline earth metals, which are having good heterogeneous nature as catalyst [8,23,42,44–51].

Lopez et al. [44] used MgO as a catalyst with calcinations temperature 600 °C and found 18% conversion of the feedstock, triacetin after 8 h of reaction time; the reason is attributed to the low surface area of the catalyst. Very recently, MgO has shown to possess catalytic activity for synthesis of biodiesel. Di Serio et al. [46,101] observed 92% biodiesel yield with MgO catalyst, using 12:1 methanol to oil molar ratio with 5.0 wt.% of the catalyst in 1 h. Dossin et al. [23] studied that MgO worked efficiently in batch reactor at ambient temperature during the transesterification reaction with a production capacity 500 tonnes of biodiesel. Biodiesel production cost is reduced in batch reactor due to the use of ambient temperature. Tateno and Sasaki [45] and Di Serio et al. [46] investigated that MgO worked well in supercritical condithions during transesterification at 300 °C in a high methanol to oil molar ratio of 39.6:1, and reported 91% of FAME yield.

2.1.2. CaO as a base heterogeneous catalyst

Among the alkaline earth metal oxides CaO is most widely used as catalyst for transesterification and report says as high as 98% FAME yield is possible during the first cycle of reaction [102]. The reactivity of such CaO is further determined by its calcinations temperature. However, reusability of catalyst for subsequent steps prevail big question mark. Modification of CaO to organo metallic nature, e.g. $Ca(OCH_3)$, $Ca(C_3H_7O_3)_2$, however, found very effective with respect to reusability. The reported literature shows the biodiesel yield as high as ∼93% even after 20 cycles of reactions. $Ca(C_3H_7O_3)_2/CaCO_3$ is also observed as an efficient heterogeneous catalyst with a reusability for 5 cycles and FAME yield as high as

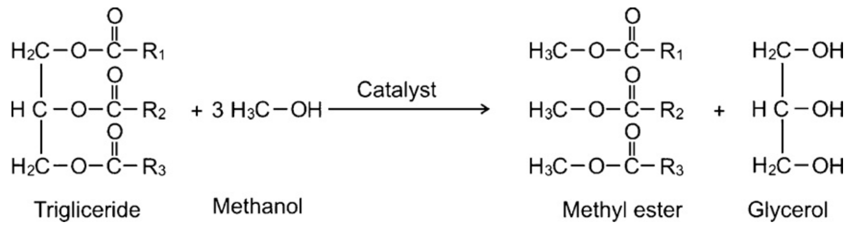


Fig. 1. Chemistry of transesterification reaction.

95% [77]. Lam et al. [31] presented the mechanism of CaO as heterogeneous base catalyst for transesterification. The basic sites of CaO were poisoned by strong adsorption of FFAs on the surface of the catalyst and consequently a portion of the catalyst changed into calcium soap by reacting with the FFAs adsorbed, resulting in low recovery of catalyst. Kouzu et al. [103] further reported that the concentration of Ca in reaction product was 3065 ppm which exceeded the basic standard of biodiesel, because the concentration of mineral matter should be below 200 ppm. Some researchers also studied that soluble substance from CaO leached out during transesterification. Gryglewicz [104] stated in his article that calcium oxide slightly dissolves in methanol and identified the soluble substance as calcium diglyceroxide in which CaO reacted with glycerol during transesterification of soybean oil with methanol. Apart from that, Granados et al. [12] used activated CaO as a solid base catalyst in the transesterification of sunflower oil to investigate the role of water and carbon dioxide on the deterioration of the catalytic performance upon contact with air for different period of time. The study showed that CaO was rapidly hydrated and carbonated in the air. After the samples were exposed to air for more than 20 days no calcium oxide peak was detected. It was further reported that the active sites of CaO were poisoned due to chemisorptions of carbon dioxide and water on the surface sites to form carbonates and hydroxyl groups, respectively. However, the catalytic activity of CaO could be regenerated if CaO is subjected to an activation treatment at 700 °C in order to remove the main poisoning species (the carbonate groups) from the surface. However, leaching of the catalyst was still observed in the transesterification reaction although prior thermal treatment was employed.

CaO has tendency to represent high basic strength and less environmental impacts due to its low solubility in methanol and can be synthesized from cheap sources like limestone and calcium hydroxide. CaO was transformed into calcium diglyceride by combining with glycerol during transesterification of soybean oil with methanol [103,106]. The surface structure of metal oxides with respect to its acidic and basic sites is as shown in Fig. 5.

CaO presented higher basicity, lower solubility, lower price, and easier to handle than KOH. However, the transesterification reaction rate is insufficient for practical applications, due to a relatively low activity [43,106]. Recently, it was reported that the catalytic activity of CaO could be improved by employing thermal activation treatment [102] and washing [106], such as calcination in order to remove the surface carbonate and hydroxyl groups. CaO is nano crystallized particle and it presented efficient characteristics as catalyst for transesterification reaction due to high surface area associated with the small crystallite sizes and defects.

Mootabadi et al. [47] investigated the ultrasonic-assisted transesterification of palm oil in the presence of alkaline earth metal oxide catalysts (CaO, SrO and BaO). Batch process assisted by 20 kHz ultrasonic cavitation was carried out to study the effect of reaction time (10–60 min), alcohol to palm oil molar ratio (3:1–15:1), catalysts loading (0.5–3%) and varying of ultrasonic amplitudes (25–100%). The activities of the catalysts were mainly related to their basic strength. The catalytic activity was in the

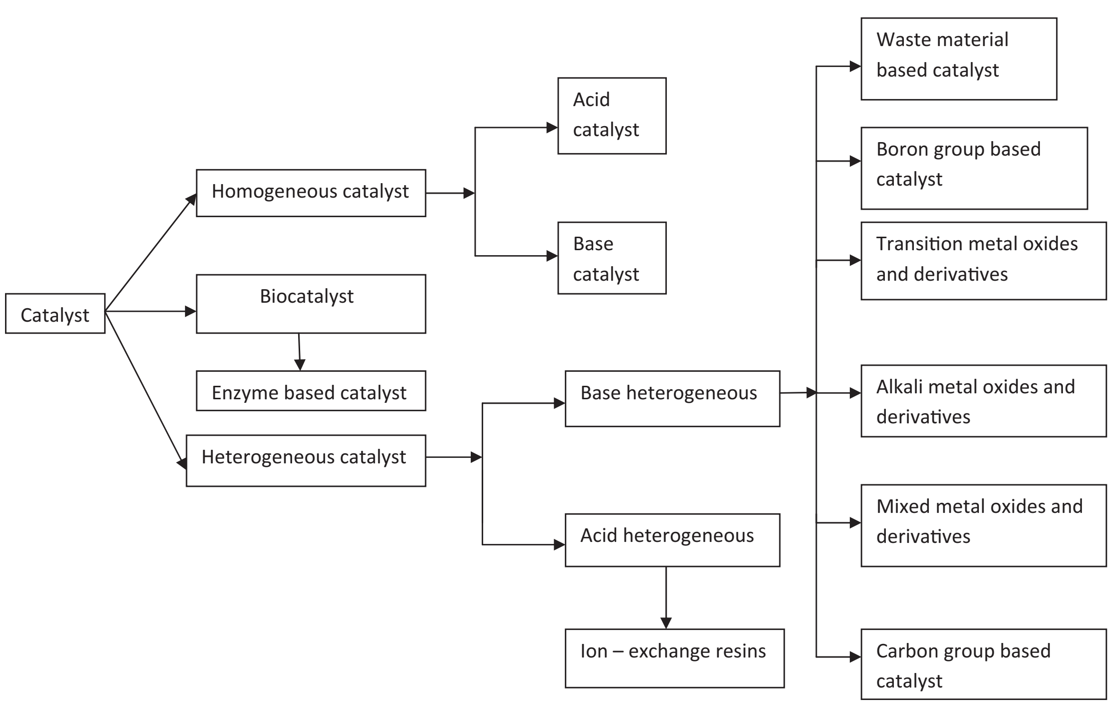


Fig. 2. Classification of catalyst.

Table 1
Heterogeneous catalytic transesterification review details.

S. No.	Title of the work	Papers included (Year)	Remarks	References
1	Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review	1984–2007	This review focused about the use of various technological methods to produce biodiesel and catalytic tranesterification	Helwani et al. [7]
2	Activity of solid catalysts for biodiesel production: a review	1993–2007	Catalyst activity had been described	Zabeti et al. [8]
3	Recent inventions in biodiesel production and processing – a review	1974–2007	This work highlighted about the recent technologies in the field of biodiesel	Sarma et al. [9]
4	Biodiesel production by heterogeneous catalysts and supercritical technologies	1987–2010	This work focused on the various new technologies of both solid catalyst and non-catalytic supercritical processes	Lee et al. [10]
5	Parametric sensitivity in transesterification of waste cooking oil for biodiesel production—a review	2002–2006	The work focused on advancements involving both esterification and transesterification for enhancing the overall yield of biodiesel	Banerjee et al. [29]
6	Latest developments on application of heterogeneous basic catalysts for an efficient and eco friendly synthesis of biodiesel: a review	2005–2010	Review focused about base heterogeneous catalyst like oxides of Mg and Ca, hydrotalcite/layered double hydroxide; alumina; and zeolites	Sharma et al. [30]
7	Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review	1998–2007	Review focused about advantages and limitations of using homogeneous, heterogeneous and enzymatic transesterification on oil	Lam et al. [31]
8	Technologies for biodiesel production from used cooking oil—a review	2002–2009	This review focused about the production and characterization of biodiesel fuel and comparison with diesel fuel	Math et al. [33]
9	Biodiesel production using heterogeneous catalysts	2003–2009	Biodiesel production using heterogeneous catalysts development of heterogeneous catalysts suitable for biodiesel production. This review help to choose suitable catalysts and the optimum conditions for biodiesel production	Semwal et al. [35]
10	Model studies in heterogeneous catalysis. From structure to kinetics	1999–2004	Efforts had made to focused about the studies on catalytic reaction kinetics at the microscopic level	Libuda et al. [38]
11	Upstream and downstream strategies to economize biodiesel production	1999–2009	This work focused about the different biodiesel production methods their advantages and disadvantage	Hasheminejad et al. [39]

sequence of CaO < SrO < BaO. At optimum conditions, 60 min was required to achieve 95% yield compared to 2–4 h with conventional stirring. Also, the yields achieved in 60 min increased from 5.5% to 77.3% (CaO), 48.2–95.2% (SrO), and 67.3–95.2 (BaO). Fifty percentage amplitude of ultrasonic irradiation was deemed the most suitable value and physical changes on the catalysts after the ultrasonic-assisted reaction were successfully elucidated. BaO catalyst underwent relatively more severe activity drop in the catalyst reusability test. Catalysts dissolution was found to be mainly responsible for activity drop of the reused catalysts, especially with BaO catalyst.

Salamatinia et al. [48] investigated the use of ultrasonic processor in the heterogeneous transesterification of palm oil for biodiesel production. Response surface methodology was employed to statistically evaluate and optimize the biodiesel production process catalyzed by two alkaline earth metal oxide catalysts, i.e. BaO and SrO. Four different variables including reaction time (10–60 min), alcohol to oil molar ratio (3:1–15:1), catalyst loading (0.5–3.0 wt.%) and ultrasonic amplitude (25–100%) were optimized. Authors developed mathematical models and predicted the behaviour of the process. The models were able to accurately predict the biodiesel yield with less than 5% error for both catalysts. The basic strength of the catalysts was the main reason for their high activities. This study confirmed that the ultrasound significantly improved the process by reducing the reaction time to less than 50 min and the catalyst loading to 2.8 wt.% to achieve biodiesel yields of above 95%. The optimum alcohol to oil ratio was found to be at 9:1 while the best amplitudes were ∼70 and ∼80% for the BaO and SrO catalysts, respectively.

Vujicic et al. [49] investigated calcium oxide as a heterogeneous catalyst and its effect on the biodiesel synthesis from refined sunflower oil. Experiments were carried out using a commercial bench stirred tank reactor of 2 dm^3 volume, at 200 rpm, with a methanol to oil ratio 6 to 1 and 1 wt.% catalyst loading as constant parameters. Ester yields were reported as a function of temperature (60–120 °C), pressure (1–15 bar) and reaction time (1.5–5.5 h). The temperature of 100 °C was found to be optimal for the maximum (91%) conversion to methyl esters, while pressure had a positive impact up to 10 bar at 80 °C. The catalyst activation in air leading to the formation of strong basic sites was found to occur at 900 °C. Catalyst particle coalescence took place during the reaction, giving a gum-like structure, and resulted in a significant catalyst deactivation. The pseudo-first order reaction was established, with a “knee” at 80 °C in the Arrhenius plot separating the kinetic and diffusion regimes. During the reaction progress, an activation energy decreased from 161 to 101 kJ/mol, and from 32 to (−3) kJ/mol, was found for the kinetic and diffusion regimes, respectively.

Yoosuk et al. [50] studied CaO prepared by a simple and flexible method for increasing the activity and improving the properties of calcined natural calcites via a hydration–dehydration approach in order to make them highly suitable for biodiesel production. The new CaO has higher surface area and amount of basic sites than CaO generated from the decomposition of calcite. The methyl ester content was enhanced to 93.9 wt.% from 75.5 wt.% with calcined

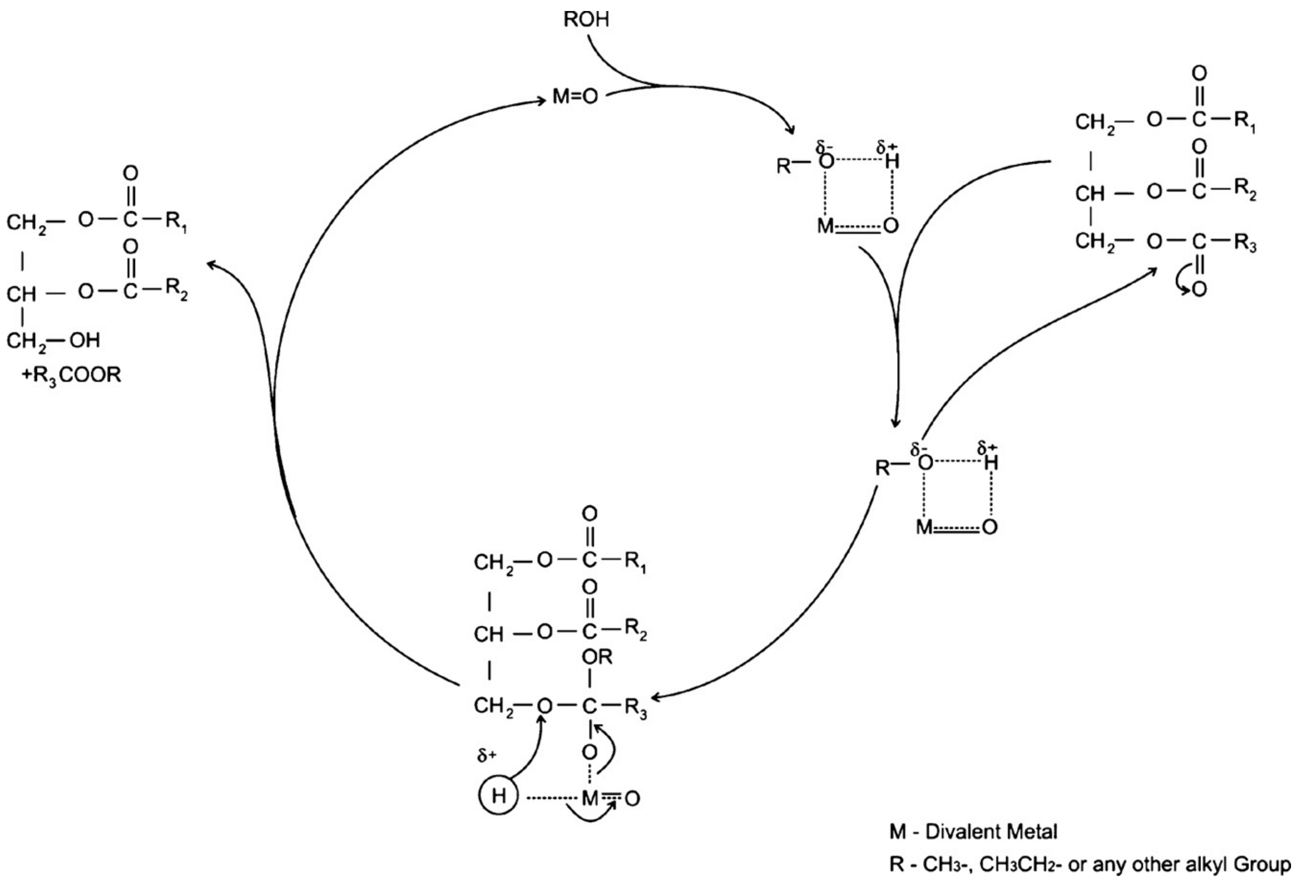


Fig. 3. Mechanism of a general base heterogeneous catalyst during transesterification.

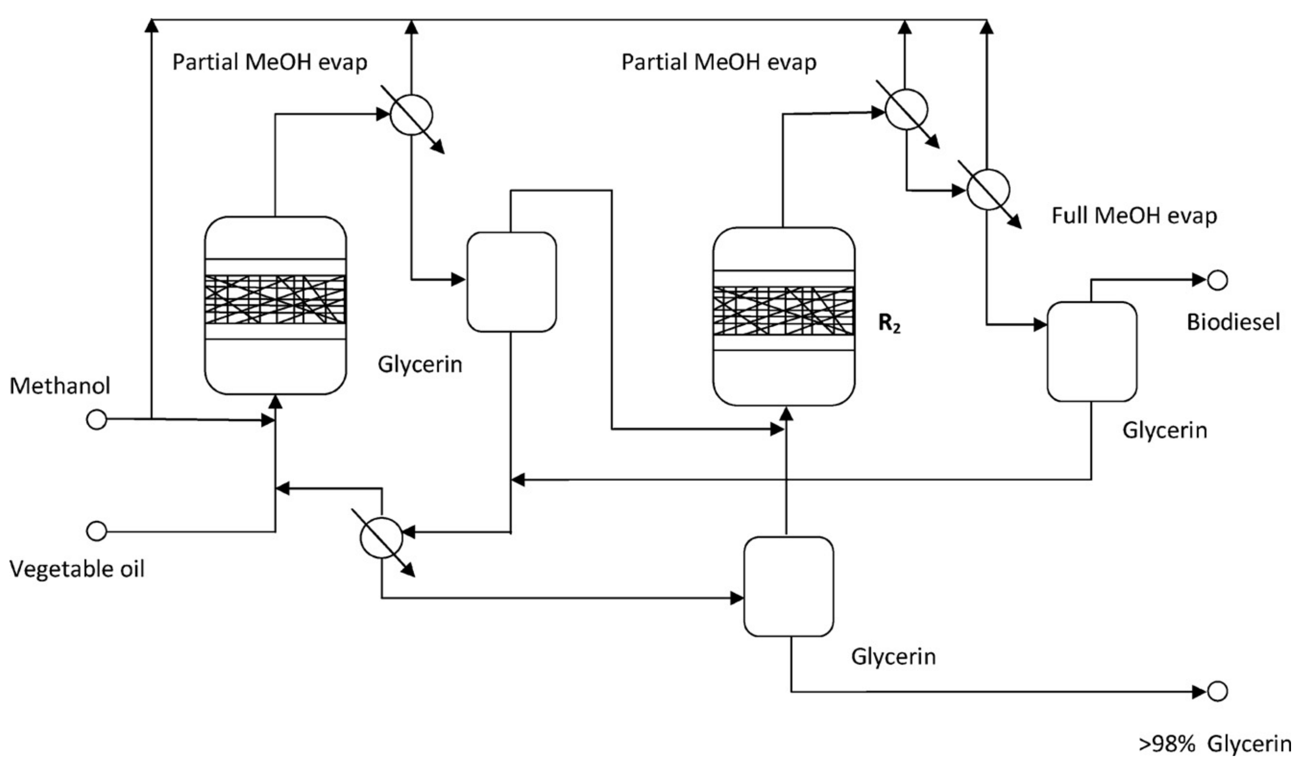


Fig. 4. Process flow diagram for biodiesel production using heterogeneous base catalyst.

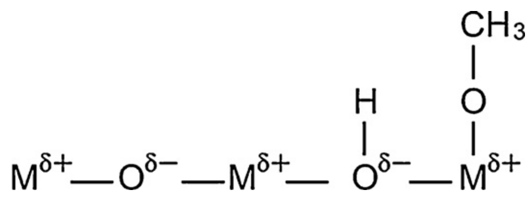


Fig. 5. Surface structure of a metal oxide.

calcite. This report provides new fundamental insight into the effect of water on properties and activity of CaO prepared by new hydration and subsequent thermal decomposition method of calcined calcite. Hai-xin et al. [59] developed a simple and low cost route for preparing the CaO with a novel morphology which could present high catalytic activity in catalyzing transesterification reaction for biodiesel. The porous CaO microsphere was synthesized by calcining spherical $CaCO_3$ precursor which was prepared easily by mixing $CaCl_2$ with Na_2CO_3. The CaO microsphere was applied in catalyzing the transesterification reaction of soybean oil and presented excellent catalytic ability with a FAME yield 98.72%.

2.1.3. Strontium oxide based catalyst

Zabeti et al. [8] indicated the suitability of using SrO as heterogeneous catalyst for transesterification. However very limited literature is available as discussed under.

Liu et al. [77] observed that SrO had high basicity and insolubility in methanol, vegetable oil and methyl esters and could be a suitable heterogeneous catalyst. They used SrO for the transesterification of soybean oil and reported 90% FAME yield in 30 min at a temperature 65 °C with alcohol/oil molar ratio of 12 and 3 wt.% catalyst loading. The reusability of the catalyst was reported to be 10 times. Yoo et al. [51] examined the synthesis of biodiesel using supercritical or subcritical methanol with metal oxide catalysts. The transesterification of rapeseed oil was carried out with the metal oxide catalysts (SrO, CaO, ZnO, TiO_2 and ZrO_2) to determine the most effective heterogeneous catalyst having the highest catalytic activity with minimum weight loss caused by dissolution. SrO and CaO dissolved in the biodiesel during the reaction because they were transformed to strontium methoxide and calcium methoxide, respectively. ZnO was the best catalyst for the transesterification of rapeseed oil owing to its high activity and minimum weight loss in supercritical methanol. The optimal reaction conditions included a molar ratio of methanol to oil 40:1 in the presence of 1.0 wt.% ZnO and a reaction time of 10 min. The supercritical process with ZnO as a catalyst appears economically viable.

A few recently published articles were selected viz. Grandos et al. [12], Wang and Yang [42], Antunes et al. [55], Illgen [68], Liu et al. [76,77], Ngamcharussrivichai et al. [98], Veljkovic et al. [102], Kouzu et al. [105], Kawashima et al. [106], Huaping et al. [108], Tafiq-Yap et al. [109], Xie et. al. [4], Encinar et al. [114], Samart et al. [115] for alkali and alkaline metal oxides and their derivatives (Fig. 6(a–e)) and depicted the role of the catalyst as a function of reaction temperature, reaction time, catalyst reusability, catalyst loading, alcohol to oil ratio and their overall impact on the product yield during transesterification.

2.2. Biodiesel production with boron groups elements

Boron group elements particularly aluminum and Al_2O_3 are extensively used loaded with various other metal oxides, halides, nitrates and alloys [3,96,107,116].

2.2.1. Boron group supported (Al_2O_3) upon CaO and MgO

Among the boron group elements boron and aluminum oxides are most commonly used for mixed metal oxide production. Al is used in the form of oxides like Al_2O_3, γ-Al_2O_3, Al_2O_3 supported upon CaO and MgO as a heterogeneous base catalyst that gives good yield of biodiesel. Xu et al. [58] used mesoporous polyoxometalate–tantalum pentoxide composite catalyst, $H_3PW_{12}O_{40}/Ta_2O_5$ which was prepared by a one-step sol–gel-hydrothermal method in the presence of triblock copolymer surfactant. On the basis of the reported research works viz. Umdu et al. [3], Xie et al. [4], Ebiura et al. [39], Arzamendi et al. [43], Antunes et al. [55], Boz et al. [60], Liang et al. [63], Furuta et al. [69], Alonso et al. [96], Barakos et al. [97], Huiping et al. [108], Shumaker et al. [116], Albequerque et al. [117], Zhang et al. [118] boron based heterogeneous catalyst can be summarized below through graphical presentations of the product yield with respect to variable parameters (Fig. 7(a–e)).

2.3. Biodiesel production with carbon group catalyst

Carbon based catalyst are easy to prepare and economically feasible heterogeneous catalysts. Shu et al. [85] used sulfonation of carbonized vegetable oil ashphalt as a solid catalyst for transesterification of vegetable oil at 220 °C, alcohol oil ratio were 16.8:1, catalyst loading 0.2%, reaction time 4.5 h and reported biodiesel yield was in the range of 80.5–94.8%. Dehkhoda et al. [87] used palm oil for transesterification reaction with KOH/AC as a heterogeneous catalyst at 70 °C and 1:1 molar ratio of alcohol to oil. The catalyst was reported to be reused upto 3 times and 94% biodiesel yield was achieved. Dehkhoda et al. [87] achieved 92% biodiesel yield from canola oil with biochar based solid acid catalyst at operating conditions: 60 °C, molar ratio of alcohol:oil 15:1, catalyst loading 5 wt.% and reaction time 15 h. Toda et al. [119] reported a sugar based carbon catalyst prepared by incineration of commercial grade sugar. However, these carbon structures could convert only 50% of oil to esters in single cycle although their catalytic activity remains the same for the next cycle.

Lou et al. [120] reported preparation of carbohydrate-derived catalysts from various D-glucose, sucrose, cellulose and starch type carbohydrates. The catalytic and textural properties of the prepared catalysts were investigated in detail and found that the starch-derived catalyst had the best catalytic performance. The carbohydrate-derived catalysts exhibited substantially higher catalytic activities for both esterification and transesterification compared to the two typical solid acid catalysts (sulphated zirconia and Niobic acid), and gave markedly enhanced yield of methyl esters in converting waste cooking oils containing 27.8 wt.% high free fatty acids (FFAs) to biodiesel. In addition, under the optimized reaction conditions, the starch-derived catalyst retained a remarkably high proportion (about 93%) of its original catalytic activity even after 50 cycles of successive re-use and thus displayed very excellent operational stability. It was clearly demonstrated that the carbohydrate-derived catalysts, especially the starch-derived catalyst, was highly effective, recyclable, eco-friendly and suitable for the production of biodiesel from waste oils containing high FFAs.

Faria et al. [121] used tetramethyl guanidine onto silica gel surface as a solid base catalyst. ^{13}C and ^{29}Si nuclear magnetic resonance details are in agreement with the proposed structure. The authors reported 86.73% biodiesel yield in 3 h of reaction time. The catalyst was recovered and reused nine times, maintaining about 62% of its catalytic efficiency.

2.4. Biodiesel production with waste materials based heterogeneous catalyst

There are several natural calcium sources such as eggshell, mollusk shell, and bones etc. widely used as raw materials for catalyst synthesis that could eliminate the wastes and simultaneously produces catalysts with high cost effectiveness. CaO catalyst derived from these waste materials could be a potential candidate for

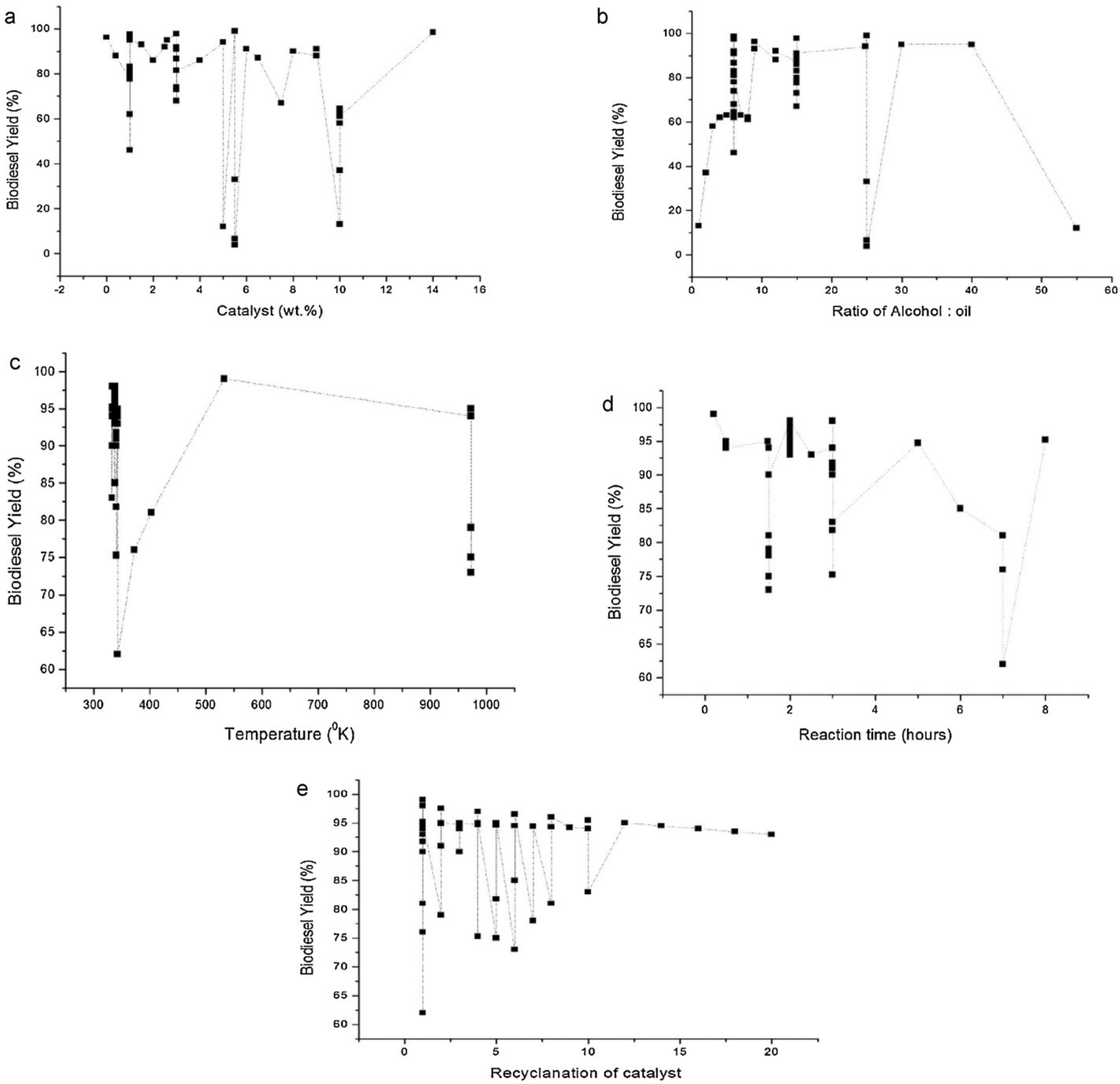


Fig. 6. Effect of boron group heterogenous catalyst. (a) Effect of catalyst on biodiesel yield, (b) Effect of ratio of alcohol: oil on biodiesel yield, (c) Effect of Temperature on biodiesel yield, (d) Effect of reaction time on biodiesel yield, (e) Effect of catalyst recyclanation on biodiesel yield.

biodiesel production. Boey et al. [2] reported the use of waste shells as a source of calcium oxide to transesterify palm olein into methyl esters (biodiesel). Characterization results revealed that the main component of the shell was calcium carbonate which transformed into calcium oxide when activated above 700 °C for 2 h. Parametric studies were investigated and optimal conditions found to be methanol/oil mass ratio, 0.5:1; catalyst amount, 5 wt.%; reaction temperature, 65 °C; and a stirring rate of 500 rpm. The waste catalyst performed equally well as laboratory CaO, thus providing another low-cost catalyst source for producing biodiesel. Reusability results confirmed that the prepared catalyst could be reused up to 11 times. Statistical analysis was performed using a Central Composite Design to evaluate the contribution and performance of the parameters on biodiesel purity.

CaO derived from waste eggshell was reported as a very effective catalyst for transesterification at 65 °C, with a oil/alcohol ratio 1:9, catalyst loading 10 wt.%, for a FAME yield 97–98%. The catalyst could be reused for 17-reaction cycle as reported [92]. Viriya-empicul et al. [91] used palm oleing oil for transesterification reaction with waste eggshell, golden apple, meretrix venus as a waste base solid heterogeneous catalyst at operational conditions were 60 °C reaction temperature, molecular ratio of alcohol:oil were 18:1, catalyst loading 10 wt.%, reaction time 1 h and carried out 97%, 83% and 78% biodiesel yield respectively. Efficient waste management and waste to energy conversion can thus fillip biodiesel production using eggshell. Du et al. [95] used soybean oil as input feedstock for biodiesel production at operating conditions 70 °C temperature, 6.9:1 molar ratio of alcohol to oil, 5 wt.% catalyst

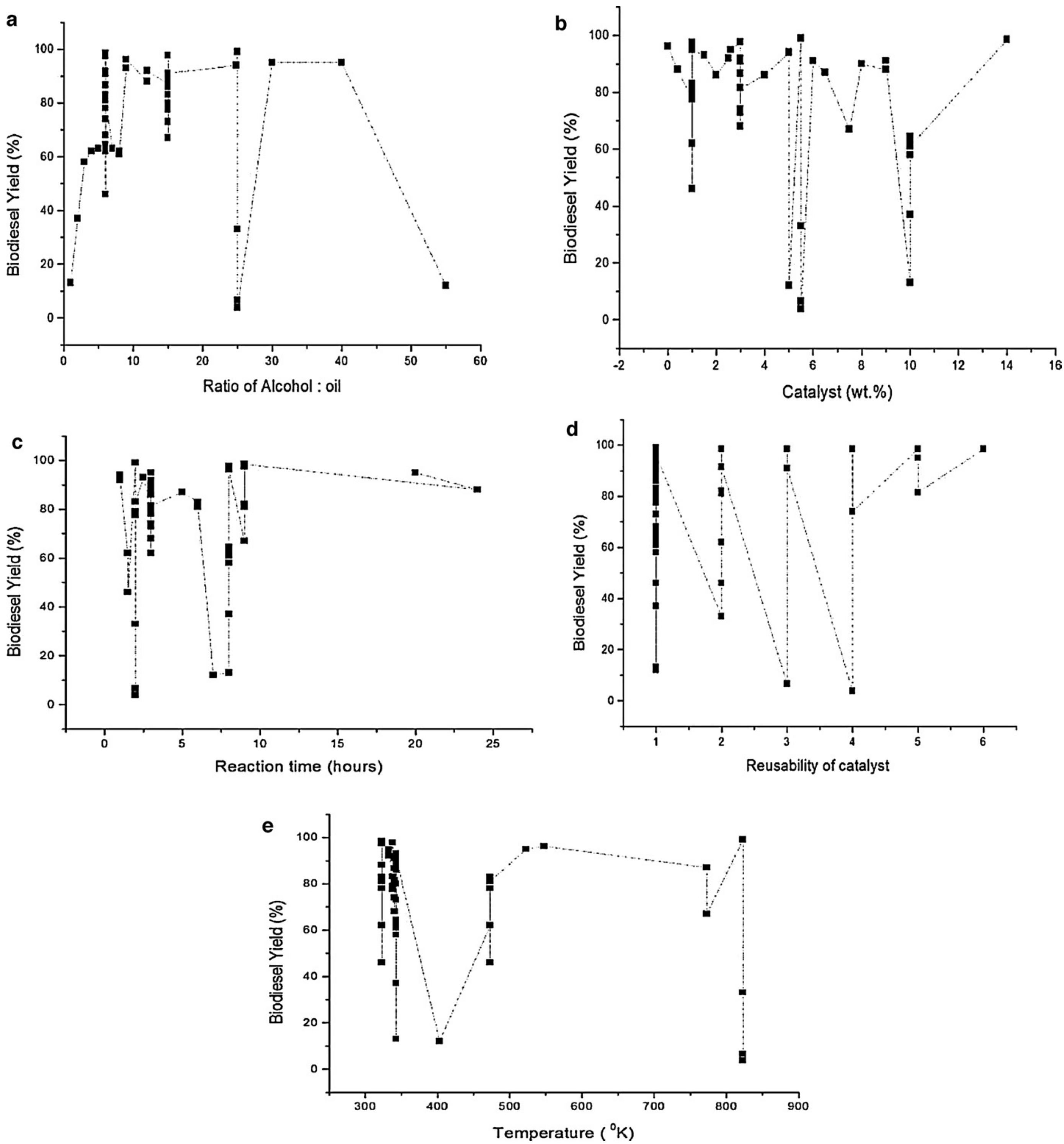


Fig. 7. Effect of alkali earth metal oxide based heterogeneous catalyst. (a) Effect of alcohol:oil on biodiesel yield, (b) effect of catalyst (wt.%) on biodiesel yield, (c) effect of reaction time on biodiesel yield, (d) effect of catalyst recyclanation on biodiesel yield, and (e) effect of temperature on biodiesel yield.

load, reaction time 5 h and catalyst could be reused upto 6 times and biodiesel yield obtained was reported as 97.73%. Nakatani et al. [122] examined transesterification of soybean oil catalyzed by combusted oyster shell.

2.5. Biodiesel production with alkali metal inserted complexes

Xie et al. [4] used soybean oil for transesterification reaction with NaX zeolites loaded with KOH as a solid heterogenous catalyst at 65 °C temperature, molar ratio of alcohol:oil 10:1, catalyst loading 3 wt.%, reaction time 8 h and reported biodiesel yield was 85.6%. Fabbri et al. [41] used soybean oil for transesterification reaction with Na_2PEG (300), dimethyl carbonate as a solid heterogenous catalyst at 70 °C temperature. The molar ratio of alcohol:oil 30:1, catalyst loading 6 wt.% and 5 h reaction time were reported for 99% biodiesel yield. Kondamudi et al. [123] synthesized special bifunctional catalysts Quntinite-3T (Q-3T) (sodium source and ammonium sources) for biodiesel production from waste vegetable

oils, restaurant grease and poultry fat that gained industrial importance compared to the high priced food based vegetable oils. This article described synthesis, characterization and catalytic activity of Quntinite-3T, a bifunctional heterogeneous catalyst that converts FFA and triglycerides (TGs) simultaneously into biodiesel. The catalyst was prepared by sol–gel process and characterized by XRD, SEM and HR-TEM. The catalyst was tested for soy, canola, coffee and waste vegetable oils with variable amounts of FFAs (0–30 wt.%). The catalyst successfully converted both FFA and TGs in a single step batch reactor.

2.6. Biodiesel production with transition metal oxides and derivatives

Among the transition metals of the periodic table researchers used mostly transition metals and their oxides viz. ZnO, TiO [51], TiO_2/SO_4^{2-} and ZrO_2/SO_4^{2-} [45], ZnO and ZrO [124–126] as base heterogeneous catalysts. The activity of zirconium oxide functionalized with tungsten oxide was also studied by Lopez et al. [127]. Nakagaki et al. [16] synthesized sodium molybdate (Na_2MoO_4) and used as a heterogeneous catalyst for the methanolysis of soybean oil. Transesterification reactions occurred under relatively mild conditions, requiring low temperatures, short reaction times and normal pressure. The methyl esters synthesized were characterized by reverse-phase and size-exclusion chromatography and hydrogen-nuclear magnetic resonance spectroscopy. The transesterification reaction of triglycerides with methanol was very efficient with yields higher than 95% methyl esters. The molybdenum(VI)-complex reported to have high Lewis acidity and most certainly act on alcohol O–H bond leading to a transient species with high nucleophilic character. The catalyst was easily recovered and after being washed showed recyclability for another catalytic reaction with similar activity.

Yoo et al. [51] carried out biodiesel production from rapeseed oil using supercritical methanol with transition metal oxides (ZnO, TiO_2 and ZrO_2). ZnO was reported the best catalyst for the transesterification of rapeseed oil owing to its high activity and minimum weight loss in supercritical methanol. The optimal reaction conditions included a molar ratio of methanol to oil 40:1 in presence of 1.0 wt.% ZnO and a reaction time of 10 min. The supercritical process with ZnO as a catalyst appeared economically viable.

Brito et al. [24] studied two series of complexes with general formula M(n-butoxide)$_{4-x}$(maltolate)$_x$, where M = Ti or Zr and x = 0–4, as catalyst for transesterification and esterification, in order to obtain methyl esters. The compounds containing different ratios of maltolate and n-butoxide ligands were synthesized from the reaction of maltol (3-hydroxy-2-methyl-4-pyrone) and n-butoxide metal precursors. All complexes, containing maltolate as ligand, were very efficient as catalyst in esterification, mainly those based in zirconium. In counterpart, these catalysts displayed very poor activity for transesterification.

Da Silva et al. [128] used two catalysts Cu(II) and Co(II) adsorbed on chitosan for transesterification of soybean and babassu oils. The catalysts were characterized by infrared, atomic absorption and TG. The biodiesel was characterized by infrared, NMR, GC, TG and physico-chemical analysis. The maximum adsorption values reported for copper and cobalt cations were 1.584 and 1.260 mg/g, respectively, in 180 min. However, conversion of oil to biodiesel was better when Co(II) was adsorbed on chitosan.

Krohn et al. [129] studied the production of algae based biodiesel using the continuous catalytic Mcgyan® process. It was demonstrated that the production of algal biodiesel from Dunaliella teriolecta, Nannochloropsis oculata, wild freshwater microalgae and macroalgae lipids were a highly efficient continuous catalytic process. In this heterogeneous catalytic process porous tatania microsphere was used in a fixed bed reactor to catalyze the simultaneous transesterification and esterification of triacylglycerides and free fatty acids, respectively, to fatty acid methyl esters (biodiesel) in presence of supercritical methanol. Triglycerides and free fatty acids were converted to alky esters up to 85% as measured by 300 MHz, HNMR spectroscopy.

Additional details about the biodiesel production with transition metal oxides and derivatives are summarized in Table 2.

2.7. Biodiesel production with mixed metal oxides and derivatives

Xu et al. [58] synthesized KF/Zn(Al)O catalyst and its catalytic activity was compared with that of Zn–Al hydrotalcite-like compounds, Zn(Al)O, KF, KF/γ-Al_2O_3 and KF/ZnO. It was found that the prepared KF/Zn(Al)O catalyst had the highest activity. This catalyst was particularly effective during transesterification for a methanol to oil molar ratio 6:1, 3 wt.% KF/Zn(Al)O catalysts loading and at 65 °C reaction temperatures the biodiesel yield exceeded 95% at a reaction time of 3 h. The high activity was ascribed to the formation of new phases KF and KOH and effect of Zn (Al)O support. Wang et al. [130] used Mgo–$MgAl_2O_4$ catalyst which was made by using γ-Al_2O_3, $MgAl_2O_4$ composite. That showed a higher biodiesel yield compared to an MgO/$MgAl_2O_4$/γ-Al_2O_3 material with the same loading of magnesium prepared by a conventional impregnation method. The enhanced catalytic activity of the former material could be ascribed to its higher basicity, specific surface area, pore volume and size. Wen et al. [131] reported kalsilite ($KAlSiO_4$), a basic silicate mineral with a framework of aluminosilicates. It contains a random network of tetrahedral Si and Al units with charge balancing alkali metal ions, conventionally produced at high pH by condensing a source of alumina and silica with an alkali silicate solution. The presence of the alkali metal ions in the crystal structure of the kalsilite prevented the leaching of the ions from the kalsilite even at relatively high temperatures. Kalsilite has macropores and strongly basic potassium active sites. These properties, along with its insolubility in vegetable oil and methanol, make kalsilite a promising candidate for transesterification of triglycerides to produce biodiesel. In this study, a coprecipitation method was used to synthesize kalsilite for transesterification of soybean oil to biodiesel. Property modification by lithium addition into the kalsilite was studied in order to improve its catalytic performance for the transesterification reaction. The authors reported that kalsilite showed relatively low catalytic activity for transesterification reaction. The catalytic activity of this catalyst was significantly enhanced by introducing a small amount of lithium nitrate by the impregnation method. A biodiesel yield of 100% with a kinematic viscosity 3.84 cSt were achieved at a mild temperature of 120 °C over this lithium modified kalsilite catalyst (2.3 wt.% Li).

On the basis of the reported research work viz. Xie et al. [4], Arzamendi et al. [43], Yang and Xie [53], Garcia et al. [54], Antunes et al. [55], Sun et al. [56], Xu et al. [58], Boz et al. [60], Kansedo et al. [62], Liu et al. [77], Baroutian et al. [86], Puna et al. [89], Alonso et al. [96], Barakos et al. [97], Ngamcharussrivichai et al. [98], Gao et al. [99], Kawashima et al. [106], Liu et al. [107], Tanfiq-Yap et al. [109], MacLeod Claire et al. [110], Wen et al. [111], Shumaker et al. [116], Albuquerque et al. [117], Faria et al. [121], Yagiz et al. [132], Caetano et al. [133], MacLeod et al. [134], Wimonrat and Suriya [135], Zeng et al. [136], Guan et al. [137], Hameed et al. [138], Sree et al. [139], Wen et al. [140], Raita et al. [141], Jiang et al. [142], DaSilva et al. [143] mixed metal oxides based heterogeneous catalyst can be summarized below through graphical presentations of the product yield with respect to variable parameters (Fig. 8(a–e)).

Di Serio et al. [46] presented the catalytic performances of several solid catalysts in the transesterification of vegetable oils with methanol in small steel vials. The eventual presence of a homogeneous contribution to the catalysis due to the leaching of the active phase was also investigated. The behaviour of one of the more

Table 2
Comparison for a few transition metal oxides used for transesterification, their reactivity, yield, selectivity and recyclability.

S. No.	Oil source	Catalyst	Temp., °C	Alcohol:oil ratio	Catalyst loading, wt.%	Reaction time, h	Biodiesel yield, %	Rec. of catalyst	Reference
1	Sunflower oil	Fe–Zn double-metal cyanide (DMC) complexes as solid catalysts.	170 °C	15:1	3	8	92.	6	[51]
2	Soybean oil	ZnO loaded with $Sr(NO_3)_2$ (alkali earth metal)	65 °C	12:1	5	1–4	94.7	NA	[52]
3	Soybean oil	$S–ZrO_2$	120 °C	20:1	5	1	98.6 (methanolysis)	4	[53]
3.1	Soybean oil	$S–ZrO_2$	120 °C	20:1	5	1	92 (ethanolysis)	4	[53]
4	Soybean oil	ZnO	130 °C	55:1	5	7	24	NA	[54]
4.1	Soybean oil	ZnO	100 °C	55:1	5	7	14	NA	[54]
4.2	Soybean oil	ZnO	70 °C	55:1	5	7	–	NA	[54]
5	Sunflower oil	ZrO_2 supported La_2O_3 catalyst (21% La_2O_3/ZrO_2)	60 °C	3:1	2	5	84.9	5	[55]

promising catalyst (TiO_2 supported on SiO_2) was further deepened in batch and continuous reactors by using the catalysts in pellets, to evaluate the possibility of developing an industrial process based on this catalyst. The catalyst life-time run, in a continuous tubular reactor, was determinant for this evaluation.

Park et al. [73] examined the tungsten oxide zirconia, sulfated zirconia and Amberlyst-15 as catalyst for a conversion of used vegetable oils (VOs) to fatty acid methyl esters (FAMEs). Among them, tungsten oxide zirconia was a promising heterogeneous catalyst for the production of biodiesel fuels from used VOs because of high activity in the conversion over 93% and no leaching of WO_3 in the esterification reaction.

Rashtizadeh et al. [144] studied the transesterification of soybean oil (TSO) with methanol. KOH was loaded on aluminosilicate layers (bentonite, kaolinite), microporous materials (zeolite Y, clinoptiloite), mesoporous materials (MCM-41, Al-MCM-41), some oxides (Al_2O_3, TiO_2, SiO_2), and silica gel as heterogeneous catalysts. Effect of reaction parameters such as KOH wt.%, amount of catalyst, reaction time, reaction temperature, molar ratio of methanol to oil and TSO yields up to 99% were reported. Utilization of bentonite and kaolinite as cheap and eco-friendly solid supports was promising.

Yu et al. [145] investigated the use of $CaO–CeO_2$ mixed oxides as solid base catalysts for the transesterification of Pistacia chinensis oil with methanol to produce biodiesel. These $CaO–CeO_2$ mixed-oxide catalysts were prepared by an incipient wetness impregnation method. The effects of reaction parameters such as the methanol/oil molar ratio, the amount of catalyst and the reaction temperature were also investigated. The best catalyst was determined as Ce 0.15–973 (with a Ce/Ca molar ratio of .15 and having been calcined at 973 K) and regenerated after five re-uses, the biodiesel yield was reported as 91%, which is slightly less than that of the fresh sample.

2.8. Biodiesel production with hydrotalcite metal oxides

Georgogianni et al. [146] reported the transesterification reaction of rapeseed oil with methanol, in the presence of alkaline catalysts, either homogeneous (NaOH) or heterogeneous (Mg MCM-41, Mg–Al Hydrotalcite, and K+ impregnated zirconia), using low frequency ultrasonication (24 kHz) and mechanical stirring (600 rpm) for the production of biodiesel. Selection of heterogeneous catalysts was based on a combination of their porosity and surface basicity. The activities of the catalysts were related to their basic strength. Mg–Al hydrotalcite showed particularly the highest activity with conversion reaching to 97%. The activity of ZrO_2 in the transesterification reaction was increased as the catalyst was doped with more potassium cations. Use of ultrasonication significantly accelerated the transesterification reaction compared to the use of mechanical stirring (5 h vs. 24 h). However, the use of homogeneous base catalysts requires neutralization and separation from the reaction mixture leading to a series of environmental problems related to the use of high amounts of solvents and energy. Heterogeneous solid base catalysts can be easily separated from the reaction mixture by simple filtration, they are easily regenerated and bear a less corrosive nature, leading to safer, cheaper and more environment-friendly operations.

Glisic et al. [147] studied several different schemes for industrial FAME production at higher pressure and temperature (catalytic or non-catalytic synthesis) was realized with the aim to find the best route to reduce the energy consumption (EC) and to improve the life cycle energy efficiency. The reported results indicated that the EC (MJ/kg FAME) mainly depends on degree of conversion of triglycerides being almost 25% lesser if degree of conversion increased from 97 wt.% to complete conversion. Further significant decrease of EC might be obtained at subcritical conditions but only after substantial decrease of methanol to oil molar ratio (from 42 to 15)

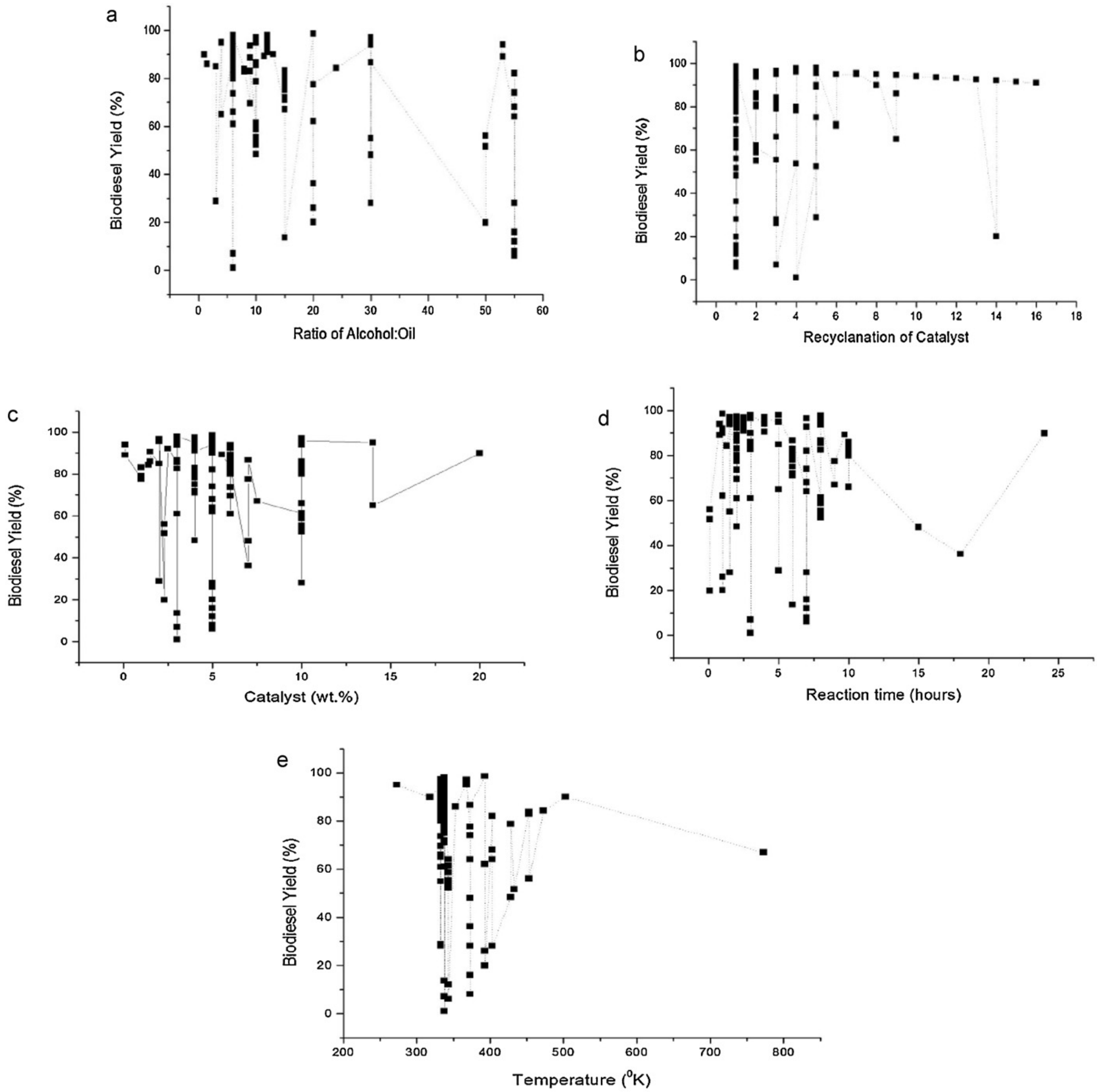


Fig. 8. Effect of mixed metal oxide derivatives heteterogenous catalyst on biodiesel production. (a) Effect of ratio of alcohol: oil on biodiesel yield, (b) Effect of catalyst recyclanation on biodiesel yield, (c)Effect of catalyst (wt. %) on biodiesel yield, (d) Effect of reaction time on biodiesel yield, (e) Effect of temperature on biodiesel yield. (Uncorrected.)

which requires use of appropriate catalyst. On account of that, the kinetics of heterogeneous catalyzed methanolysis of triglycerides was reportedly analysed using data published in literature (CaO) as well as own experimental data (K_2CO_3/Al–O–Si) with a goal to obtain reliable kinetic rate constant which might be used for process simulation. This study revealed that if heterogeneous process of biodiesel synthesis is realized at subcritical conditions then further decrease of EC is possible.

2.9. Zeolite based catalysts

Zeolites as catalyst have the characteristics of acidic sites and shape selectivity. Zeolites vary in pore structures, inner electric fields from crystal and surface properties attributed to their varying catalytic properties. Zeolite can accommodate a wide variety of cations such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+} and many others, that attributed to its basic nature.

Suppes et al. [148] studied zeolites as the potential heterogeneous catalyst for the preparation of biodiesel. A variety of zeolites and metals were utilized as catalysts for transesterification of soybean oil possessing free fatty acid (2.6%).

Xie et al. [4] studied NaX zeolites as a heterogeneous catalyst. NaX catalyst (Si/Al = 1.23) after loading with KOH increased the basic strength from <9.3 to 15.0–18.4. The conversion reported was moderate (85.6%) by 10% loading of KOH on NaX beyond which its activity decreased owing to agglomeration of active KOH phase

and/or the coverage of active base sites. The catalyst was reused after washing with cyclohexane and heating for 2 h at 125 °C. The conversion of the methyl esters then decreased to 48.7%, which was attributed to leaching of KOH. However, when the catalyst was regenerated by impregnation method, the yield obtained was 84.3%, which was comparable to the initial yield achieved. The low conversion obtained with the catalyst indicated the presence of tri-, di-, and monoglycerides which makes the biodiesel fuel off specification.

Ramos et al. [149] used zeolites (mordenite, beta, and X) as a heterogeneous catalysts for transesterification of sunflower oil that gave methyl ester yields as high as 93.5–95.1 wt.% at 60 °C reaction temperature. When the leaching studies were carried out, sodium was found to have leached in the mixture, giving the reaction a homogeneous pathway. However, metal incorporation on the catalyst was observed to be far superior with the widely used impregnation method than with the ion-exchange method. This was attributed to the absence of strong basic sites on the catalyst by the ion-exchange technique. However, the method employed for the preparation of the catalyst was longer. This required heating, drying, and calcining at 500 °C for 10 h, 120 °C for 12 h, and 550 °C for 15 h respectively.

Marchetti and Errazu [21] used zeolites as catalysts for conversion of high FFA oils to FAME. NaY zeolites (basic in nature) and VOx over Ultra Stable Y zeolite (USY) (acidic in nature) calcined at 300 °C for 3 h showed conversion oil to biodiesel in just 10 min and 50 min, respectively, and had been reported as potential alternates to homogeneous catalysts for esterification. Presence of water had a positive influence at the start of the reaction and negative influence later when the reaction proceeded further and thus lowering the final conversion.

Chung et al. [150] studied removal of FFA from waste frying oil by esterification with methanol using various zeolite catalysts. The ZSM-5 (MFI), modern site (MOR), fauja site (FAU), beta (BEA) zeolites, and silicalite were employed with different Si/Al molar ratio in the reaction. The effects of acidic properties and pore structure of the zeolite catalysts were discussed relating to the conversion of the FFA. The MFI zeolite induced an improvement of the removal efficiency of FFA by cracking to the FFA in its pore structure due to its narrow pore mouth. The catalytic activity for FFA removal was lowered with decreasing of acid strength of the zeolites. The strong acid sites of zeolites induced the high conversion of FFA. The acid strength and pore structure of acidic zeolites affected the catalytic activity in FFA removal.

3. Chemistry of acid heterogeneous catalyst

Currently, biodiesel research is focused on exploring new and sustainable solid acid catalysts for transesterification reaction. In addition, it is believed that solid acid catalysts have the strong potential to replace liquid acid catalyst [72]. The advantages of using solid acid catalyst are (1) they are insensitive to FFA content, (2) esterification and transesterification occurs simultaneously [113], (3) eliminate the washing step of biodiesel [124], (4) easy separation of the catalyst from the reaction medium, resulting in lower product contamination level, (5) easy regeneration and recycling of catalyst and (6) reduce corrosion problem, even with the presence of acid species [151]. In fact, the development of heterogeneous catalyst system holds an important factor to be incorporated into a continuous flow reactor [152]. Such continuous process can minimize product separation and purification costs, making it economically viable and able to compete with commercial petroleum-based diesel fuel [79], the ideal solid acid catalyst for transesterification reaction should have characteristics such as an interconnected system of large pores, a moderate to high concentration of strong acid sites, and a hydrophobic surface [113]. However, research on direct use of solid acid catalyst for biodiesel production has not been widely explored due to its limitation of slow reaction rate and possible undesirable side reactions. Furthermore, there is a knowledge gap on the fundamental studies dealing with reaction pathway of triglycerides on solid acids. The following section will give an overview of various solid acid catalysts reported so far for biodiesel production. The reaction mechanism of an acid heterogeneous catalyst is depicted in Fig. 9.

3.1. ZrO_2 as acid heterogeneous catalyst

There have been several studies on ZrO_2 as a heterogeneous acid catalyst for transesterification of different feedstock due to its strong surface acidity. Jitputti et al. [124] reported that SO_4^{2-}/ZrO_2 could produce promising results in transesterification of palm kernel oil and crude coconut oil with methyl ester yield reaching as high as 90.3% and 86.3%, respectively. However, when unsulfated ZrO_2 was used as catalyst instead of SO_4^{2-}/ZrO_2, only 64.5% (palm kernel oil) and 49.3% (crude coconut oil) of methyl ester yield were reported, respectively. This eventually indicates that modification of metal oxide surface acidity is the key factor in obtaining high conversion of triglycerides. Apart from that, combination of alumina, Al_2O_3 with ZrO_2 and modification of ZrO_2–Al_2O_3 with tungsten oxide (WO_3) not only provides high mechanical strength but also enhances the acidity of the catalyst Jacobson et al. [72]. The addition of Al_2O_3 further stabilizes the tetragonal phase of ZrO_2 support and also prevents the growth of WO_3 particles. Furuta et al. [69] evaluated the performance of tungstated zirconia–alumina (WZA) and sulfated zirconia–alumina (SZA) in the transesterification of soybean oil with methanol at 200–300 °C using a fixed bed reactor under atmospheric pressure. WZA was found to have a higher activity in transesterification as compared to SZA. However, the authors did not elaborate much on the causes of the improved activity of WZA catalyst. Nevertheless, high reaction temperature (250 °C) and long reaction time (20 h) were needed in order to achieve 90% conversion. Similar results were also reported by Park et al. [73], where by catalyst was prepared by impregnating 10 wt.% of WO_3 on to ZrO_2–Al_2O_3. Relatively low ester yield was obtained (65%) when the transesterification reaction was carried out at lower reaction temperature of 200 °C and shorter reaction time of 10 h [75]. On the other hand, Faria et al. [121] proposed a reaction mechanism for ZrO_2 supported on SiO_2 in transesterification of soybean oil, as shown in Fig. 9. Thus, a more detail understanding on reaction pathway by ZrO_2 catalyst in transesterification can be obtained. Application of ZrO_2 in esterification of waste cooking oil was also reported by Park et al. [73]. In their study, WO_3 was incorporated into ZrO_2 rather than impregnating with H_2SO_4. It was found that WO_3/ZrO_2 has higher stability than SO_4^{2-}/ZrO_2, and therefore avoiding the leaching of acid sites into the reaction media. Even if WO_3 leached into the reaction media, it does not contaminate the product. In their study, it was found that 85% of FFA conversion was attained in a packed-bed reactor after 20 h of reaction time at 75 °C, but decreased to 65% and remained stable thereafter. The reason given was due to the oxidation of WO_3 after long term exposure to FFA (a reducing agent) that resulted to a decrease in catalytic activity. Therefore, leaching of WO_3 was rule out as the main reason for catalyst deactivation. In addition, WO_3/ZrO_2 could be simply regenerated by air re-calcination. However, further study on catalyst, process optimization and also the oxidation state of WO_3 are still required [74,152].

Sulfated zirconia (SZ) was synthesized by Muthu et al. [153] in a solvent free method which was used to prepare Neem Methyl Ester (Biodiesel) by a two-step process of esterification and transesterification from Neem oil. Acid catalyst was used for the esterification and alkali catalyst (KOH) for the transesterification reaction. Opti-

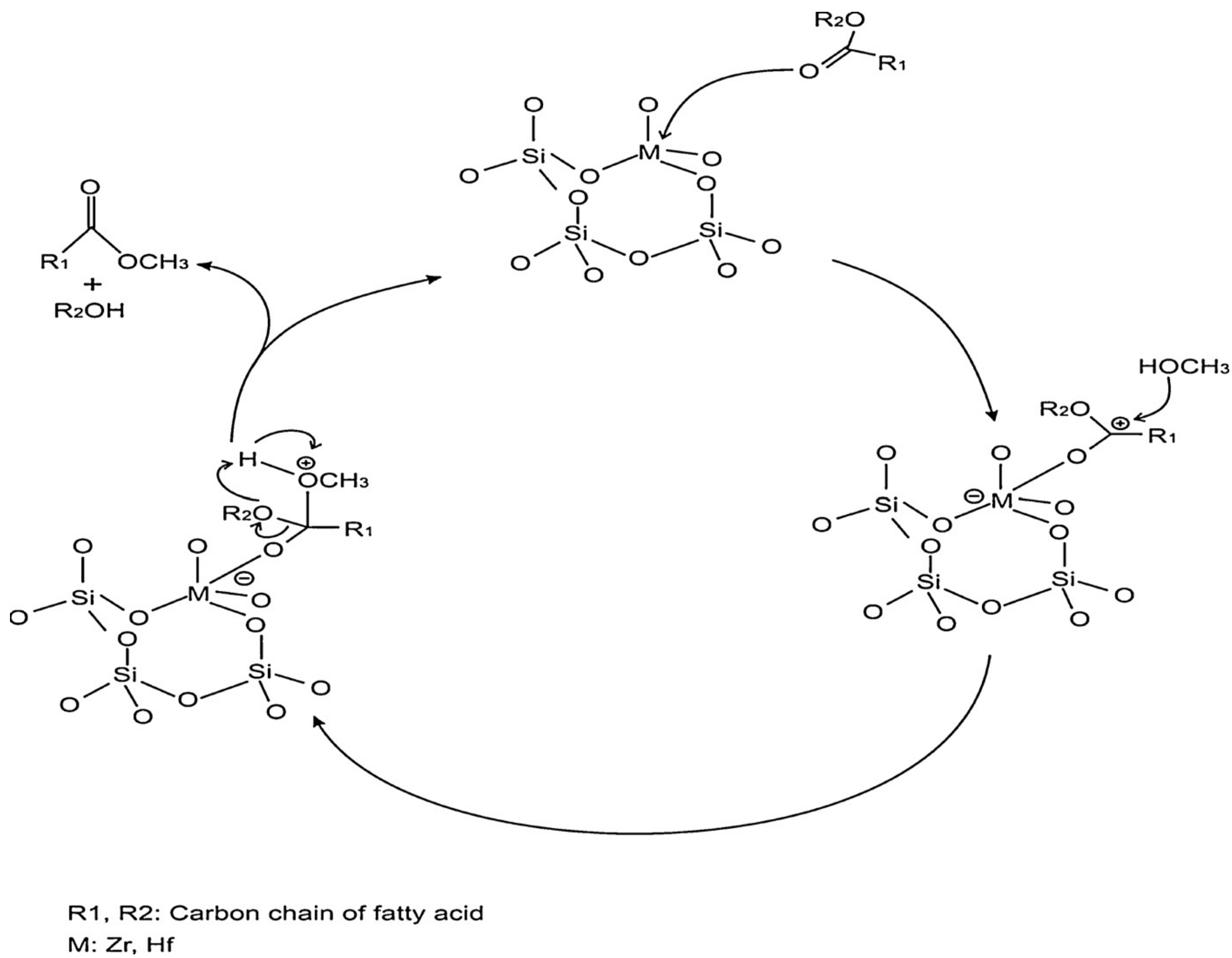


Fig. 9. Chemical mechanism of acid heterogeneous catalyst.

mal Free Fatty Acid (FFA) conversion was achieved using 1 wt.% SZ as an acid catalyst with a methanol-to-oil molar ratio of 9:1, temperature of 65 °C and reaction time of 2 h. The acid value was reduced to 94% of the raw oil (24.76 mg KOH/g), which confirmed the conversion. Consequently, this pretreatment reduces the overall complexity of the process and a conversion efficiency of 95% was reported when pretreated oil reacts with methanol in the presence of KOH.

3.2. Cation-exchange resin as a heterogeneous catalyst

Cation-exchange resins are reported extensively for laboratory scale biodiesel preparation although industrial application is not yet explored. Liang et al. [63] synthesized new and feasible $[Et_3NH]Cl–AlCl_3$ catalyst for the production of biodiesel. The chloroaluminate ionic liquid selected for the synthesis of biodiesel was very efficient for the reaction under the operating conditions: catalyst $[Et_3NH]Cl–AlCl_3$ ($x(AlCl_3) = 0.7$), soybean oil 5 g, methanol 2.33 g, reaction time 9 h, temperature 70 °C. They reported 98.5% biodiesel yield. Operational simplicity, low cost of the catalyst used, high yields, no saponification and reusability were the key features of this methodology. Zhang et al. [118] studied the transesterification of zanthoxylum bungeanum seed oil (ZSO) containing high free fatty acids (FFA) using ferric sulfate followed by transesterification using calcium oxide (CaO) as an alkaline catalyst. Acid value of ZSO with high FFA could be reduced to less than 2 mg KOH/g by one-step esterification with methanol-to-FFA molar ratio 40.91:1, ferric sulfate 9.75% (based on the weight of FFA), reaction temperature 95 °C and reaction time 2 h that could satisfy transesterification using an alkaline catalyst. The response surface methodology (RSM) was used to optimize the conditions for ZSO biodiesel production using CaO as a catalyst. A quadratic polynomial equation was obtained for biodiesel conversion by multiple regression analysis and verification experiments confirmed the validity of the predicted model. The optimum combination for transesterification was methanol-to-oil molar ratio 11.69:1, catalyst amount 2.52%, and reaction time 2.45 h. At this optimum condition, the yield of biodiesel was reported to be 96%. This study provided a practical method for biodiesel production from raw feedstocks with high FFA with high reaction rate, less corrosion, less toxicity, and less environmental problems.

Giri et al. [154] reported esterification of palmitic acid on ammonium salt of 12-tungstophosphoric acid (TPA). The influence of ammonium content of the acid was investigated by preparing partially and fully proton exchanged catalysts. Potentiometric titration method was employed for the quantification of their acidity. The partially exchanged catalyst, possessing stronger acidic sites, was found to be more active than its fully exchanged analogue.

Hamad et al. [155] presented heterogeneized heteropolyacids, $H_3PW_{12}O_{40}/SiO_2$ and $Cs_2HPW_{12}O_{40}$ as catalysts for transesterification of rapeseed oil with ethanol in mild conditions. The number and the strength of the acid sites were evaluated by calorime-

try. Over anhydrous $H_3PW_{12}O_{40}$ and $Cs_2HPW_{12}O_{40}$, acid sites of homogeneous strength with heat of ammonia adsorption near 200 kJ/mol were measured. By contrast, $H_3PW_{12}O_{40}/SiO_2$ showed sites of lower strength with a heterogeneous distribution. The catalytic activity did not correlate the acid strength of solid catalysts. Indeed, equivalent TOF were determined on $H_3PW_{12}O_{40}$ and silica supported $H_3PW_{12}O_{40}$ while lower TOF were measured on microporous $Cs_2HPW_{12}O_{40}$. The TOF values were interpreted in terms of leaching of the active phase in the case of $H_3PW_{12}O_{40}/SiO_2$ while reduced acid sites accessibility might explain the lower TOF measured on $Cs_2HPW_{12}O_{40}$.

Katada et al. [156] used a heteropoly acid-derived solid acid catalyst, $H_4PNbW_{11}O_{40}/WO_3^-$ Nb_2O_5 calcined at 773 K (HPNbW/WNb). That showed a higher catalytic activity for transesterification between triolein and ethanol into ethyloleate compared to the activities of conventional solid acid catalysts. The catalyst HPNbW/W-Nb was insoluble to the reaction mixture, while such heteropoly acids as $H_4PNbW_{11}O_{40}$ and $H_3PW_{12}O_{40}$ showed high activities but were dissolved into the reaction mixture. The activity was sensitive to calcinations temperature, and calcination around 773 K provided a highly active catalyst. The reaction rate showed the maximum at 10–30 of the ethanol/triolein molar ratio. The activity was observed in the co-presence of water and oleic acid. The reaction rate was high when methanol was used in place of ethanol. In a fixed-bed continuous-flow reaction, its potential as an insoluble catalyst was suggested by its stable activity during at least 4 days of the reaction.

Kolaczkowski et al. [157] studied the transesterification reaction of triglycerides with alcohols using a zinc amino acid complex $[ZnL_2]$ as a catalyst. This was fixed onto a structured monolith support (cordierite), so as to enable the catalysts to be retained in a fixed bed. To advance this work, reaction experiments were performed in a 120 ml batch reactor, using 10 mm × 10 mm × 10 mm sections of catalyst coated monolith (1.1 mm square channels, 62 cells cm^{-2}). It was reported that 54% of the triglyceride was converted into biodiesel with a 12:1 molar ratio of methanol and rapeseed oil (triglyceride), at 195 °C and 20 bar, and using 0.3 g of zinc catalyst (coated on a monolith). This result was found very interesting with a conversion of 69% in batch experiments, when 0.3 g of the catalyst was dispersed in the solution in the form of a very fine powder. Interestingly, it was also shown, that the cordierite monolith support on its own exhibited catalytic activity (27% conversion of the triglyceride).

Li et al. [158] reported lab scale process for clean, facile and ecologically friendly biodiesel production from Eruca Sativa Gars (ESG) vegetable oil. Transesterification of ESG oil was heterogeneously catalyzed by $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ heteropolyacid salt. The properties of biodiesel so obtained were comparable to conventional diesel fuel and compared with the US Standard for Biodiesel (ASTM 6751). Using ESG biodiesel instead of conventional diesel fuel reduces emissions. The results illustrated that the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is an environmentally benign solid acid catalyst.

Carmo et al. [159] carried out esterification of palmitic acid with methanol, ethanol and isopropanol in the presence of Al-MCM-41 mesoporous molecular sieves with Si/Al ratios of 8, 16 and 32 as catalysts. The catalytic acids were synthesized at room temperature. The reaction was carried out at 130 °C while stirring at 500 rpm, with an alcohol/acid molar ratio of 60 and 0.6 wt.% catalysts for 2 h. The alcohol reactivity follows the order methanol > ethanol > isopropanol. The catalyst Al-MCM-41 with ratio Si/Al = 8 produced the largest conversion values for the alcohols studied. The data followed a rather satisfactory approximation to first-order kinetics. Feng et al. [160] used three types of cation-exchange resins (NKC-9, 001 × 7 and D61) as solid acid catalysts to prepare biodiesel from acidified oils generated from waste frying oils. The results unveil that catalytic activity of NKC-9 was higher than that of 001 × 7 and D61. The conversion of the esterification by NKC-9 increased with increasing the amount of catalyst, reaction temperature and time and methanol/oil molar ratio. The maximal conversion was reportedly 90.0%. Furthermore, NKC-9 resin exhibits good reusability. Gas chromatography–mass spectrometry analysis revealed that the production was simple and mainly composed of C16:0 (palmitic), C18:2 (linoleic), and C18:1 (oleic) acids of methyl esters, respectively. Lam et al. [31] investigated heterogeneous acid catalyst for transesterification of oil with high free fatty acid (FFA). However, the immiscible phases of methanol-oil-catalyst in the initial reaction mixture usually lead to slow reaction rate and long reaction time. To overcome this difficulty, the use of biodiesel as co-solvent for transesterification reaction catalyzed by SO_4^{2-}/SnO_2–SiO_2 (solid acid catalyst) was investigated. It was found that with the use of biodiesel as co-solvent, a high FAME yield of 88.2% (almost 30% higher than without using co-solvent) could be obtained in a shorter reaction time (1.5 h) using the following reaction conditions; reaction temperature 150 °C, methanol to oil ratio of 15 and catalyst loading of 6 wt.% (weight of oil).

Cannila et al. [161] reported the results obtained using a novel MnCeOx system in the transesterification reaction of refined sunflower oil with methanol. The performance of such catalysts was compared with that of common acid supported catalysts. Results obtained revealed that MnCeOx system possessed a superior activity especially by operating at low temperatures (≤120 °C). Chen and Fang [162] reported a novel catalyst prepared by sulphonation of glucose–starch mixture. Experiments showed that solid acid had the highest esterification activity when glucose and corn powder were mixed at ratio of 1:1, carbonized at 400 °C for 75 min and sulfonated with concentrated H_2SO_4 (98%) at 150 °C for 5 h. The catalyst was characterized by acid activity measurement, XPS, TEM and FT-IR. The results indicated that solid acid ($CS_{0.073}O_{0.541}$) composed of both Lewis acid sites and Bronsted acid sites caused by $-SO_3H$ and –COOH. The conversions of oleic acid and triolein to esters after transesterification were reported 96% and 60%, respectively. Biodiesel production from waste cottonseed oil containing high free fatty acid (FFA 55.2 wt.%) using this catalyst was reported and the methyl ester yield was found 90% after 12 h. The catalyst deactivated gradually after recycles usage, but it could be regenerated by H_2SO_4 treatment.

Corro et al. [163] carried out transesterioficationl from waste frying oil (WFO) in two steps catalyzed process. The free fatty acids (FFA) were first esterified with methanol catalyzed by SiO_2 pretreated with HF. The catalyst was easy to recover; neither hydrated nor carbonated, did not dissolved by the reactants or the products of the reaction, showed high activity for the FFA esterification and presented high stability. After 10 esterification runs, the catalyst activity remained unchanged. During the second step, the triglycerides WFO were transesterified with methanol catalyzed by NaOH. Gas chromatography and mass spectrometry analysis revealed that the process proposed in this investigation led to a biodiesel containing 96% methyl esters. The process may thus be regarded as heterogeneous–homogeneous catalytic process. Some more information for cation exchange resin as heterogeneous catalyst is summarized in Table 3.

3.3. Biodiesel production with sulfated oxides as an acid heterogeneous catalyst

Jackson et al. [75] studied the organosulfonic acid-functionalized mesoporous silica and were tested for catalytic performance in the esterification of oleic acid with metanol in flowing supercritical carbon dioxide. The energy of activation of the sulfonic acid catalysts was found to be about 42 kJ/mol and was shown to be independent of pore size. The catalytic activity of the functionalized silica was compared to a standard acidic resin,

Table 3
Comparison for a few cation exchange resins used for transesterification, their reactivity, yield, selectivity and recyclability.

S. No.	Oil source	Catalyst	Temp., °C	Alcohol:oil ratio	Catalyst loading, wt%	Reaction time, h	Biodiesel conversion yield, %	Rec. of catalyst	Ref.
1	Soybean oil	TiO_2/ZrO_2	175–200 °C	1:40	4.0	4–20	95	NA	[68]
2	Methyl soyate	Ruthenium catalysts	40 °C	–	0.1	2	46	–	[69]
3	Methyl soyate	(SAC-13) sulfuric acid and a commercial Nafion/silica composite solid acid catalyst	60 °C		0.5–3				[69]
4	Sunflower oil	Basic resin	45 °C	6.128:1	2–5	–	80	–	[21]
5	Waste cooking oil	The zinc stearate immobilized on silica gel (ZS/Si)	200 °C	18:1	3	10	98	4	[71]
6	Vegetable oils	WO_3/ZrO_2 catalyst	75 °C	19.4:1	0.2	1	70	3	[72]
7	Oil	Trifluoroacetic acid	120 °C	20:1		5	98.4	–	[143]
8	Jatropha curcas oil	Sulfated tin oxide (SiO_2 ($SO_4^{2-}/SnO_2–SiO_2$))	60–80 °C	15:1	3	2	97	–	[141]
9	Free fatty acid (FFA) in acidified oil	Zirconium sulfate ($Zr(SO_4)$)	–	–	–	–	94.5	–	[142]
10	Free fatty acid (FFA) in acidified oil	Sulfonated poly(vinyl alcohol) (SPVA)	–	–	–	–	81.2	–	[142]

Amberlyst 15, and to an immobilized lipase, Novozym 435. The most active catalyst was Novozym 435. Liu et al. [76] investigated the impact of carboxylic acid chain length on the kinetics of liquid-phase acid-catalyzed esterification using sulfuric acid and a commercial Nafion/silica composite solid acid catalyst (SAC-13). Initial kinetics was measured for the reactions of a series of linear chain carboxylic acids (acetic, propionic, butyric, hexanoic, and caprylic acid) with methanol at 60 °C. It was found that reaction rate decreased as the number of carbons in the linear alkyl chain increased for both H_2SO_4 and SAC-13. There were important parameters, such as water deactivation, catalyst reusability, and regeneration, which were also affected by the size of the carboxylic acid. SAC-13 underwent significantly more activity loss with subsequent reaction cycles as the size of the alkyl tail on the carboxylic acid increased. Characterization of the catalyst after the reaction ascertained that the deactivation of SAC-13 was caused likely by the entrapment of bulky reaction intermediates on Nafion polymeric nano domains. Zhu et al. [83] employed poly(styrene sulfonic acid) (PSSA)/poly(vinyl alcohol) (PVA) blend membranes prepared by the solution casting as heterogeneous acid catalysts for biodiesel production from acidic oil obtained from waste cooking oil (WCO). The membranes were annealed at different temperature in order to enhance their stability. The structure and properties of the membranes were investigated by means of Fourier transform infrared spectroscopy (FTIR), thermogravimetry (TG), X-ray diffraction (XRD). It is found that the cross linking structure among PVA and PSSA chains formed when the thermal treatment temperature was higher than 80 °C. The retention of PSSA in the blend membranes in the methanol/water solvent was markedly increased from 50% to 85% with the increase of the annealing temperature from room temperature (for the untreated membrane) to 150 °C due to the formation of the cross linking structure. The results of esterification of acidic oil showed that the conversion was slightly improved with the PVA content in the membrane at a fixed PSSA content. The thickness of the catalytic membrane had no significant effect on the conversion. The membrane annealed at 120 °C exhibited the best catalytic performance among the membranes, with a stable conversion of 80% with the runs.

Shi et al. [164] synthesized a novel organic–inorganic hybrid membrane as heterogeneous acid catalyst for biodiesel production from zirconium sulfate ($Zr(SO_4)_2$) and sulfonated poly(vinyl alcohol) (SPVA). The structure and properties of the hybrid catalytic membrane were investigated by means of Fourier transform infrared spectroscopy (FTIR), differential scanning calorimeter (DSC), thermogravimetry (TG), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The catalytic performance of the hybrid membranes was tested by the esterification of the acidified oil with methanol. It was found that the $Zr(SO_4)_2$ particles were better dispersed in SPVA matrix as a result of the stronger interaction between $Zr(SO_4)_2$ and SPVA compared with $Zr(SO_4)_2$/poly(vinyl alcohol) (PVA) hybrid membrane. Esterification results showed that the conversions of free fatty acid (FFA) in acidified oil were 94.5% and 81.2% for $Zr(SO_4)_2$S/PVA and $Zr(SO_4)_2$/PVA catalytic membranes, respectively. The stability of $Zr(SO_4)_2$/SPVA catalytic membrane is superior to $Zr(SO_4)_2$/PVA catalytic membrane.

Zhang et al. [165] used an efficient microwave-assisted transesterification (MAT) technique to prepare biodiesel from yellow horn (Xanthoceras sorbifolia Bunge.) oil with a heteropolyacid (HPA) catalyst namely $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. A study for optimizing the reaction conditions such as reaction temperature, time, molar ratio of methanol/oil, catalyst amount, and recycle number of catalyst was reported. The maximum yield of fatty acid methyl esters (FAMEs) reached to 96.22% under optimal conditions: temperature 60 °C, reaction time10 min, molar ratio of methanol/oil 12:1, 1% (w/w of oil) catalyst and minimum recyclability nine times. The

final product of biodiesel obtained after the new catalyzed process was analyzed by gas chromatography. The results showed that the $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ heterogeneous acid catalyst had higher efficiency for transesterification under microwave irradiation as compared with the conventional method. The properties of yellow horn biodiesel are found to be in agreement with EN 14214 Standard. Some information's on biodiesel production with sulfated oxides as acid heterogeneous catalysts are summarized in Table 4.

4. Acid–base heterogeneous catalyst

Heterogeneous catalysts having both acidic and basic sites had been investigated which could simultaneously esterify FFA and transesterify triglycerides (TG) to biodiesel. Sun et al. [56] used acid-catalyzed esterification and transesterification reactions, suitable for biodiesel production from high acid value oils. In this study, authors developed a two-step process for fast acid-catalyzed biodiesel production from high acid value oil in a micro structured reactor, which was assembled with an SIMM-V2 micro mixer connected with a 0.6 mm i.d. stainless steel capillary. Esterification of oleic acid and transesterification of cottonseed oil with methanol were separately carried out to depict suitable reaction conditions. The influences of the residence time, the methanol to acid/oil molar ratio, the catalyst concentration, the water/acid concentration and the reaction temperature were examined. The highest oleic acid conversion was obtained when esterification of oleic acid with methanol was carried out at 100 °C with the residence time of 5 min, while the highest yield of fatty acid methyl ester (FAME) was achieved when transesterification of cottonseed oil with methanol was conducted at 120 °C with the residence time of 20 min. Thereafter, a two-step process was developed based on the above reaction conditions with the first and second steps separately conducted under the esterification and transesterification reaction conditions. The results indicated that the acid value of the acid oil was reduced from 160 to 1.1 mg KOH/g with a methanol to acid molar ratio of 30, the H_2SO_4 concentration of 3 wt.%, a residence time of 7 min at 100 °C in the first step. The final FAME yield reached 99.5% with a methanol to triglyceride molar ratio of 20, the H_2SO_4 concentration of 3 wt.%, a residence time of 5 min at 120 °C in the second step. Therefore, biodiesel production from high acid value oil could be continuously achieved at high yields by acid-catalyzed transesterification in microstructured reactors with total reaction times of less than 15 min.

Perin et al. [78] reported microwave assisted transesterification of castor oil. Transesterification reaction was performed in the presence of methanol or ethanol, using a molar ratio alcohol/castor bean oil of 6:1, and 10% (w/w) of acidic silica gel or basic alumina (in relation to the oil mass) as catalyst. Under acid catalysis, the reaction occurred with satisfactory yields using H_2SO_4 immobilized in SiO_2, methanol under conventional conditions (60 °C for 3 h) as well as using microwave irradiation for 30 min. The best results were obtained under basic conditions (Al_2O_3/50% KOH) using methanol and conventional (60 °C, stirring, 1 h) or microwave conditions (5 min). In comparison with conventional heating, the catalyzed alcoholysis assisted by microwaves is much faster and leads to higher yields of the desired fatty esters. Lin et al. [166] patented for preparation of mesoporous calcium, magnesium silicate and barium silicate by co-condensation method, by forming a mixed oxide from strong basic metal oxide and weak acidic silica. In calcium silicates mixed oxide, silica sites were lewis acidic, Ca sites as basic and hydroxyl group on surface acted as Brönsted acids.

Lin and Liun [167] reported the synthesis of mixed metal oxide mesoporous silica material for TG transesterification and simultaneous esterification of FFA. They prepared these meso-

Table 4
Comparison for a few sulfated oxides used for transesterification, their reactivity, yield, selectivity and recyclability.

S. No.	Oil source	Catalyst	Temp., °C	Alcohol:oil ratio	Catalyst loading, wt.%	Reaction time, h	Biodiesel conversion yield, %	Rec. of catalyst	Ref.
1	Methyl soyate	Ruthenium catalysts	40	–	0.1	2	46	–	[69]
	Methyl soyate	(SAC-13) sulfuric acid and a commercial Nafion/silica composite solid acid catalyst	60		0.5–3	2	46	–	[69]
2	Ethyl propanoate and ethyl hexanoate	Heteropoly acids (H_2SO_4, Amberlyst-15 and zeolites HY and H-Beta)	60	20:1	0.1	1	84	2	[70]
3	Waste cooking oil	The zinc stearate immobilized on silica gel (ZS/Si)	200	18:1	3	10	98	4	[71]
4	Vegetable oils	WO_3/ZrO_2 catalyst	75	19.4:1	0.2	1	70	3	[72]
5	Soybean and castor oils at	Superacid sulfated titania catalyst, TiO_2/SO_4 (TS-series)	120	–	–	1	25–40	–	[76]
6	Crude palm oil	Sulfonic acid-functionalized SBA-15	140	20:1	6	4	95	–	[177]
7	Sunflower oil/methanol mixtures	Silica functionalized with 4-ethyl-benzene sulfonic acid groups	200	6:1	1.5	–	–	–	[157]
8	Oleic acid	Lipozyme CALB	Room temperature	–	–	–	98	–	[21]

porous calcium silicate mixed metal catalysts having different amount of calcium oxide. A co-condensation method was used for preparation in which cetyltrimethyl ammonium bromide (CTAB) provided the micelles template in a NaOH catalyzed reaction of tetraethylorthosilicate (TEOS) and the metal oxide. The catalyst after isolation was freed from surfactant CTAB by calcination at 600 °C for 6 h. These catalysts could esterify soybean oil in methanol in 24 h (80 °C) and could also esterify the free acids. The recovered catalysts could be reused 30 times for transesterification and 8 times for esterification without significant loss of catalyst activity. Lin and Radu [168] reported three catalysts, having different Ca/Si ratios, and were able to transesterify soybean oil at 90–100% conversion level. The effective temperature range was claimed to be 80 °C and complete conversion took more than 26 h. Under similar conditions complete esterification of poultry fat acids could be achieved in 24 h. All the catalysts were evaluated for recyclability's and no loss of activity was noticed in 20 cycles.

Jitputti et al. [124] studied several acidic and basic solids as catalysts, such as ZrO_2, ZnO, SO_4^{2-}/SnO_2, SO_4^{2-}/ZrO_2, KNO_3/KL zeolite and KNO_3/ZrO_2 as heterogeneous catalysts for crude palm kernel oil (PKO) and crude coconut oil (CCO) transesterification with methanol. It was found that ZnO and SO_4^{2-}/ZrO_2 exhibited the highest activity for both PKO and CCO transesterification. In the case of SO_4^{2-}/ZrO_2, only 1 wt.% of this acidic solid was needed to catalyze the reaction, and resulted in fatty acid methyl esters content higher than 90%. Moreover, a study of the catalyst's recyclability indicated that the spent SO_4^{2-}/ZrO could not be directly reused for the transesterification. However, this spent catalyst could be easily regenerated and the same activity could be obtained.

Macario et al. [169] reported biodiesel production by homogeneous/heterogeneous catalytic system of acid–base type. First the acid catalyst, both strong acid type USY, BEA and weak acid catalyst of the type MCM-41 were prepared by hydrothermal synthesis procedures. Later, for preparation of acid–base type catalyst, potassium (K) was loaded on different materials by ionic exchange methods. For K loading, the calcined catalyst materials were treated with 1 M KCl solution at 80 °C and the ratio of solid/solution was kept at 0.01 g/ml. These K loaded samples were calcined again at 300 °C for 8 h. Transesterification reactions were carried out at 100 to 180 °C, molar ratio of oil to methanol at 1:20, and using 5 wt.% of catalyst. At the end of reaction, the catalyst was separated by centrifugation, washed with water and dried overnight at 120 °C. It was observed that strong acid catalysts like USY, BEA was not good for triglyceride conversion and commercial potassium silicate was found to be much better. The K loading of MCM-41 increased the conversion of triglyceride to a great extent but biodiesel production was low as the main products were FFA (32%), mono-glycerides (42%). The K loaded delaminated zeolites (K ITQ-6) gave 97% triglyceride conversion and biodiesel yield of 80%, under the similar reaction conditions. However, when the recovered catalyst was recycled, a sharp decrease in biodiesel yield was observed and had been attributed to leaching of K from the catalyst.

5. Biocatalyst

Rathore and Madras [19] reported the use of Novozym-435 lipase for biodiesel production from pongamia pinnata and jatropha curcas in presence of supercritical carbon dioxide. The effect of reaction variables such as temperature, molar ratio, enzyme loading and kinetics of the reaction were investigated for enzymatic synthesis in supercritical carbon dioxide. Very high conversions (>80%) were obtained within 10 min and nearly complete conversions were reported within 40 min for the synthesis of biodiesel in supercritical alcohols. However, conversions of only 60–70% were obtained in the enzymatic synthesis even after 8 h under normal circumstances. Yagiz et al. [132] reported waste oils transesterification with lipase immobilized on hydrotalcite and zeolites catalyst under the reaction conditions: catalyst loading 4 wt.%, molar ratio of methanol to oil 4:1, reaction time 5 h. The reported biodiesel yield was 95% even after 7th cycle of the reaction. Raita et al. [141] used palm oil for biodiesel production with catalyst Novuzymes 435 (immobalized C. antarctica lipase B) and Lipotase 100T (granulated silica immobilized T. languginosous lipase), catalyst loading 20 wt.%, molar ratio of oil alcohol 1:4, reaction time 24 h and biodiesel yield 89.9% and catalyst recyclability was 4–8 times.

Nassreddine et al. [170] studied commercial lipase solution from Candida antartica, Lipozyme1 encapsulated in silica aerogels reinforced with silica quartz fibre felt. This biocatalyst was applied in biodiesel synthesis by direct transesterification of sunflower seed oil with methanol, without any other solvent. With a molar ratio1 for methanol to oil, the encapsulated enzyme achieved ∼90% methanol conversion after ∼50 h at 40 °C. The recycling activity increased by ∼40% after the first test, then slowly decreased in the next runs to reach an activity still 20% higher than the initial during the fifth test. Textural and structural analysis of the aerogels before and after catalytic tests showed improvement associated with a modification of the liquid medium inside the aerogel by preferential adsorption of glycerol. The aerogel samples were also compared to a commercial CALB product immobilized on polymer beads with a different enzyme loading, from Fluka. This product showed a better activity during the first test but its activity decreased by ∼20% during the second test.

Suwannakarn et al. [171] presented the activity and stability of a commercial SZ catalyst for the liquid-phase transesterification of triglycerides at 120 °C. The kinetics of tricaprylin (TCP) transesterification with a series of aliphatic alcohols (methanol, ethanol, and n-butanol) was investigated at 120 °C and 6.8 atm in a Parr batch reactor. It was reported that the catalytic activity for TCP conversion decreased as the number of carbons in the alkyl chain of alcohol increased, most likely as a result of increased steric hindrance. The SZ catalyst exhibited significant activity loss with subsequent reaction cycles. The characterization of used catalysts after their exposure to various alcohols at 120 °C showed that the SO_4^{2-} moieties in SZ were permanently removed. The SO_4^{2-} species were leached out, most likely as sulfuric acid, which further reacted with alcohols to form monoalkyl and dialkyl sulfate species, as demonstrated by ^{1}H NMR studies. This was in essence the main route for catalyst deactivation. Our findings conclusively demonstrate for the first time that in alcoholic liquid media at higher temperatures, SZ deactivates by leaching of its active sites, most likely leading to significant homogeneous rather than heterogeneous catalysis.

Wang et al. [172] investigated biodiesel production from corn oil catalyzed by lipozyme TL IM, an inexpensive 1,3-position specific lipase from thermomyces lanuginosus. They optimized the process by response surface methodology (RSM) and a central composite rotatable design (CCRD) was used to study the effects of enzyme dosage, ratio of t-butanol to oil (v/v) and ratio of methanol to oil (mol/mol) on the methyl esters (ME) yield during the methanolysis. The optimum combinations for the reaction were 25.9 U/goil of enzyme, 0.58 volume ratio of t-butanol to oil and 0.5, 0.5, 2.8 molar equivalent of methanol to oil added at the reaction time of 0, 2, and 4 h, respectively, for a ME yield of 85.6%. Waste oil was found to be more suitable feedstock, and could give 93.7% ME yield under the optimum conditions described above. Adding triethylamine (TEA), an acylmigration enhancer, could efficiently improved the ME yield of the methanolysis of corn oil, giving a ME yield of 92.0%.

Xi and Davis [173] synthesized magnesium–aluminum hydrotalcite with an Mg/Al molar ratio of 4 by a coprecipitation method. Thermally decomposed and rehydrated Mg–Al hydrotalcites were used to catalyze the transesterification of tributyrin, a model triglyceride, with methanol (by tributyrin:km molar ratio 1:30)

at 333 K to produce methyl butyrate, monobutyrin, dibutyrin, and glycerol. The pseudo first order rate constants of a three-step reaction sequence for tributyrin transesterification were determined by fitting a kinetic model to the experimental data. Although decomposed and rehydrated Mg–Al hydrotalcite was one order of magnitude more active than decomposed Mg–Al hydrotalcite based on surface area measured by N_2 adsorption, the activity correlated well to the CO_2 adsorption capacity. The most active rehydrated samples were also deactivated faster, presumably because butyric acid produced by hydrolysis of ester with adsorbed water reacted with the basic sites. The areal rate and CO_2 adsorption capacity of decomposed-rehydrated Mg–Al hydrotalcite decreased as the interlayer water was removed by heating.

Brun et al. [174] reported the synthesis of the first lipase [C-CRl]@Glymo-Si(HIPE) and [C-TAl]@Glymo-Si(HIPE) hybrid macrocellular biocatalysts. The authors studied optimization of crude enzyme immobilization while circumventing the reactants' low kinetic diffusion by the use of silica macroporous hosts. As a direct consequence, these new hybrid biocatalysts displayed unprecedented cycling catalytic performance, as demonstrated by the syntheses of butyloleate ester (used as biodiesel lubricant), hydrolysis of linoleic-glycero ester derivatives (end products used for detergent and soap generations), and trans-esterification (reaction involved in the synthesis of low viscosity biodiesel). Considering that the catalytic performances were given in terms of absolute conversion percentage and not just relative enzyme activity, the enzyme@Glymo-Si(HIPE) hybrid macrocellular biocatalysts presented in the study displayed unprecedented high yield cycling catalytic performances, where turnover numbers (TON) and turnover frequencies (TOF) showed promise for real industrial applications.

Winayanuwattikun et al. [175] used 27 types of plants found to contain more than 25% of oil (w/w) were selectively examined from 44 species. The authors characterized oils different parameters such as saponification number (SN), iodine value (IV), cetane number (CN) and viscosity (Z) of fatty acid methyl esters (FAMEs) of the respective oils. Fatty acid compositions, IV, CN and Z were used to predict the quality of FAME. FAMEs of plant oils of 15 species were found to be most suitable for use as biodiesel by meeting them or specification of biodiesel standards of Thailand, USA and European Standard Organization. The oils from these 15 species were further investigated for their conversion to biodiesel in a lipase-catalyzed transesterification reaction with Novozyme435 and Lipozyme RMIM. Oils of four species, palm (Elaeis guineensis), physic nut (Jatrophacurcas), papaya (Carica papaya) and rambutan (Nephelium lappaceum), could beefficiently converted to biodiesel by transesterification using Novozyme435- or Lipozyme RMIM-immobilized lipaseas catalyst. Therefore, these selected plants seed oil could be economically considered as the feedstock for biodiesel production using biocatalyst.

Park et al. [176] carried out the production of fatty acid methyl esters (FAMEs) from triglyceride embedded in waste activated bleaching earth (ABE) discarded by the crude oil refining industry using lipase from Candida cylindracea in a 50-L pilot plant. Diesel oil or kerosene was used as an organic solvent for the transesterification of triglycerides. When 1% (w/w) lipase was added to waste ABE, the FAME content reached 97% (w/w) after reaction for 12 h at 25 °C with an agitation rate of 30 rpm. The FAME production rate was strongly dependent upon the amount of enzyme added. Mixtures of FAME and diesel oil at ratios of 45:55 (BDF-45) and 35:65 (BDF-35) were assessed and compared with the European specifications for biodiesel as automotive diesel fuel, as defined by pr EN 14214. The biodiesel quality of BDF-45 met the EN 14214 standard. BDF-45 was used as generator fuel, and the exhaust emissions were compared with those of diesel oil. The CO and SO_2 contents were reduced, but nitrogen oxide emission increased by 10%. This is the first report of a pilot plant study of lipase-catalyzed FAME production using waste ABE as a raw material. This result demonstrated a promising reutilization method for the production of FAME from industrial waste resources containing vegetable oils for use as a biodiesel fuel.

6. Summary and conclusion

Heterogeneous catalysts are reported at length in literature for the laboratory scale biodiesel production. Among the alkaline earth metal oxides CaO is most widely used as catalyst for transesterification and report says as high as 98% FAME yield is possible during the first cycle of reaction. The reactivity of such CaO is further determined by its calcinations temperature. However, reusability of catalyst for subsequent steps prevail big question mark. Modification of CaO to organo metallic natures, e.g. $Ca(OCH_3)$, $Ca(C_3H_7O_3)_2$ however found very effective with respect to reusability. The reported literature shows the reactivity as high as ∼93% even after 20 cycles of reactions. $Ca(C_3H_7O_3)_2/CaCO_3$ is also observed as the efficient heterogeneous catalyst with a reusability for 5 cycles and FAME yield as high as 95%. Nano-MgO was reported as a good catalyst and a maximum of 99% yield of FAME is possible. However no reported data are available for its reusability for subsequent steps. SrO was extensively used for laboratory scale biodiesel production and up to 94.9% FAME yield was reported. Reusability after 10 cycles was also reported and FAME yield as high as 94% were observed by various researchers. These imply SrO could be a potential heterogeneous catalyst for biodiesel industry. Dolomite on the other hand is reported to be less effective as catalyst after 9th cycle of reaction at 60 °C temperature.

Activated carbon using KOH as activator are also reported in literature with FAME yield 94% and reusability for 3 cycles of reaction. CaO derived from waste eggshell was reported as a very effective catalyst for transesterification at 65 °C, with a oil/alcohol ratio 1:9, catalyst loading 10 wt.%, for a FAME yield 97–98%. The catalyst could be reused for 17-reaction cycle as reported. Efficient waste management and waste to energy conversion can thus fillip biodiesel production using eggshell. As a solid catalyst derived from waste fish (*Labeo Rohita*) has also the potential to substitute homogenous catalyst with a reusability of 6 cycles of reaction and FAME yield as high as 97.73%.

Alkali metal inserted complexes are also found in literature, e.g. Na_2PEG (300) dimethyl carbonate that shows 99% FAME yield in an oil:alcohol ratio 1:30 within 5 h at 60 °C. However reusability of catalyst was never mentioned. Chloro aluminate ionic liquid is a prominent heterogeneous catalyst for transesterification under the boron group oxides and derivatives. As high as 98.5% FAME yield is possible at 60 °C with a reusability factor of 6 cycles.

Among the transition metal oxides Fe–Zn double metal cyanide complexes shows some promising results with ester yield 92.2% at 150 °C and reusability of catalyst for 6 cycles. Similarly S-ZrO_2 catalyst was found quite satisfactory at high alcohol to oil molar ratio and 98.6% FAME yield was reported even after 4 cycles of reaction at 120 °C. ZrO_2 supported with La_2O_3 was reportedly an effective catalyst at 60 C for 1:3 molar ratio of oil to alcohol and could be reused up to the 5 cycles with FAME yield as high as 84.9%.

CaO supported on mesoporous silica shows high proficiency in the first reaction cycle for conversion of sunflower oil to FAME (95% yield) after 5 h reaction. Hydrotalcite and zeolite immobilized with lipase were reported as efficient catalyst for transesterification reaction at NTP with an alcohol oil molar ratio 4:1, reaction time 5 h. The catalyst could be reused upto 7 cycles without much decrease of reactivity for subsequent cycles. Mixed Ca and Zn oxides catalysts have also the potential to substitute conventional alkali catalyst during biodiesel production at high alcohol oil molar ratio (30:1).

However, the catalyst requires calcinations at 800 °C for subsequent steps and as high as 97% FAME may be obtained even after fourth cycle of reaction. Instead the catalyst could be reused after washing with methanol and 5 M NH_4OH solution and dried to achieve 96% FAME yield after 5th cycle of reaction. KF loaded with nano γ-Al_2O_3 catalyst could transesterify canola oil to 97% FAME in a high alcohol oil molar ratio (20:1) upto 5 cycles of reactions at 65 °C. Mixed KF/CaO could be very attractive heterogeneous catalyst at 12:1 molar alcohol oil ratio, with 4% catalyst loading at 65 °C for 2.5 h and was established for Chinese tallow seed oil with repeatability for 16 cycles to achieve biodiesel yield 97–91%.

SO_4^{2-}/ZrO_2 could produce promising results in transesterification of palm kernel oil and crude coconut oil with methyl ester yield reaching as high as 90.3% and 86.3%, respectively. Chloroaluminate ionic liquid was reported as a very efficient catalyst for biodiesel preparation under the operating conditions: catalyst $[Et_3NH]Cl$–$AlCl_3$ ($x(AlCl_3) = 0.7$), soybean oil 5 g, methanol 2.33 g, reaction time 9 h, temperature 70 °C for 98.5% biodiesel yield. Ion exchange resin could be another efficient catalyst for industrial application among the acidic catalyst with suitable reusability. Trifluroacetic acid is another potential heterogeneous catalyst for industrial scale biodiesel production. The zinc stearate immobilized silica gel is reported as good catalyst at high temperature (200 °C), high alcohol oil molar ratio (18:1) and 3% catalyst loading for 3 h to achieve biodiesel yield 98% and catalyst reusability for 4-cycles. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ catalyst assisted with microwave showed some good results during transesterification. Acid base heterogeneous catalyst could be effective for high free fatty acid containing oil for two step transesterification reactions.

Lypoenzyme CALB is reportedly an effective catalyst for transesterification of pure oleic acid. However, the catalytic activity diminishes in the subsequent batch ~20%. Lypoenzyme TL IM is reportedly an effective catalyst for waste oil with 93% biodiesel yield. However main snag of using biocatalyst is the slow reactivity and very high reaction time required for transesterification. It is expected that heterogeneous catalyst may be intriguing a position in commercial biodiesel production in a very near future.

Acknowledgement

Authors are highly thankful to the Ministry of New and Renewable Energy, Govt. of India for all kinds of help and funding (Sanction F No. 7/144/2009-NT dt. 01.10.2010).

References

[1] Meher LC, Sagar DV, Naik SN. Technical aspects of biodiesel production by transesterification: a review. Renew Sustain Energy Rev 2006;10:248–68.
[2] Boey PL, Maniam GP, Hamid SA. Biodiesel production via transesterification of palm olein using waste mud crab (Scylla serrata) shell as a heterogeneous catalyst. Bioresour Technol 2009;100:6362–8.
[3] Umdu ES, Tuncer M, Seker E. Transesterification of nannochloropsis oculata microalgas lipid biodiesel on Al_2O_3 supported CaO and MgO catalysts. Bioresour Technol 2009;100:2828–31.
[4] Xie W, Huang X, Li H. Soybean oil methyl esters preparation using NaX zeolites loaded with KOH as a heterogeneous catalyst. Bioresour Technol 2007;98:936–9.
[5] Ma F, Hanna MA. Biodiesel production: a review. Bioresour Technol 1999;70:1–15.
[6] Wang Y, Wang X, Liu Y, Ou S, Tan Y, Tang S. Refining of biodiesel by ceramic membrane separation. Fuel Process Technol 2009;90:422–7.
[7] Helwani Z, Othman MR, Aziz N, Kim J, Fernando WJN. Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review. Appl Catal A: Gen 2009;363:1–10.
[8] Zabeti M, Wan M, Wan D. Activity of solid catalysts for biodiesel production: a review. Fuel Process Technol 2009;90:770–7.
[9] Sarma AK, Sarmah JK, Barbora L, Kalita P, Chatterjee S, Mahanta P, et al. Recent inventions in biodiesel production and processing: a review. Recent Patent Eng 2008;2:47–58.
[10] Lee JS, Saka S. Biodiesel production by heterogeneous catalysts and supercritical technologies: review. Bioresour Technol 2010;101:7191–200.
[11] Canakci M, Van Gerpan J. Biodiesel production from oils and fats with high free fatty acids. Trans ASAE 2001;44:1429–36.
[12] Grandos ML, Poves MD, Alonso D, Mariscal R, Galisteo FC, Moreno-Tost R, et al. Biodiesel from sunflower oil by using activated calcium oxide. Appl Catal B: Environ 2007;73:317–26.
[13] Ji J, Wang J, Li Y, Yu Y, Xu Z. Preparation of biodiesel with the help of ultrasonic and hydrodynamic caviation. Ultrasonics 2006;44:411–4.
[14] Kumar KS, Anju C. Preparation of biodiesel from crude oil of Pongamia pinnata. Bioresour Technol 2005;96:1425–9.
[15] Van Gerpen J. Biodiesel processing and production. Fuel Process Technol 2005;86:1097–107.
[16] Nakagaki S, Bail A, dos Santos VC, de Souza VHR, Vrubel H, Nunes FS, et al. Use of anhydrous sodium molybdate as an efficient heterogeneous catalyst for soybean oil methanolysis. Appl Catal A: Gen 2008;351:267–74.
[17] Dizge N, Aydiner C, Imer DY, Bayramoglu M, Tanriseven A, Keskinler B. Biodiesel production from sunflower, soybean, and waste cooking oils by transesterification using lipase immobilized onto a novel microporous polymer. Bioresour Technol 2009;100:1983–91.
[18] Sivozhelezova V, Bruzzeseb D, Pastorinoa L, Pechkova E, Nicolini C. Increase of catalytic activity of lipase towards olive oil by Langmuir-film immobilization of lipase. Enzyme Microb Technol 2009;44:72–6.
[19] Rathore V, Madras G. Synthesis of biodiesel from edible and non-edible oils in supercritical alcohols and enzymatic synthesis in supercritical carbon dioxide. Fuel 2007;86:2650–9.
[20] West AH, Dusko D, Ellis N. Assessment of four biodiesel production processes using HYSYS. Plant Bioresour Technol 2008;99:6587–601.
[21] Marchetti JM, Errazu AF. Comparison of different heterogeneous catalysts and different alcohols for the esterification reaction of oleic acid. Fuel 2008;87:3477–80.
[22] Sakai T, Kawashima A, Koshikawa T. Economic assessment of batch biodiesel production processes using homogeneous and heterogeneous alkali catalysts. Bioresour Technol 2009;100:3268–76.
[23] Dossin TF, Reyniers MF, Berger RJ, Marin GB. Simulation of heterogeneously MgO-catalyzed transesterification for fine-chemical and biodiesel industrial production. Appl Catal B: Environ 2006;67:136–48.
[24] Brito YC, Mello VM, Cesar C, Macedo CS, Meneghetti MR, Suarez AZ, et al. Fatty acid methyl esters preparation in the presence of maltolate and n-butoxide Ti(IV) and Zr(IV) complexes. Appl Catal A: Gen 2008;351:24–8.
[25] Islon AP, MacRae AR, Smith CG, Bosley J. Mass transfer effects in solvent free intersterification reactions – influences on catalyst design. Biotechnol Bioenergy 1994;43:122–30.
[26] Miao S, Shanks BH. Esterification of biomass pyrolysis model acids over sulfonic acid – modified mesoporous silicas. Appl Catal A 2009;359:113–20.
[27] Sharma YC, Singh B, Upadhyay SN. Advancements in development and characterization of biodiesel: a review. Fuel 2008;87:2355–73.
[28] Sharma BK, Suarez Paulo AZ, Perez JM, Erhan SZ. Oxidation and low temperature properties of biofuels obtained from pyrolysis and alcoholysis of soybean oil and their blends with petroleum diesel. Fuel Process Technol 2009;90:1265–71.
[29] Banerjee A, Chakraborty R, Banerjee A. Parametric sensitivity in transesterification of waste cooking oil for biodiesel production—a review. Resour Conserv Recycl 2009;53:490–7.
[30] Sharma YC, Singh B, Korstad J. Latest developments on application of heterogeneous basic catalysts for an efficient and eco friendly synthesis of biodiesel: a review. Fuel 2011;90:1309–24.
[31] Lam MK, Lee KT, Mohamed AR. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review. Biotechnol Adv 2010;28:500–18.
[32] Sawangkeaw R, Bunyakiat K, Ngamprasertsith S. A review of laboratory scale research on lipid conversion to biodiesel with supercritical methanol (2001–2009). J Supercrit Fluids 2010;55:1–13.
[33] Math MC, Kumar SP, Soma V, Chetty SV. Technologies for biodiesel production from used cooking oil—a review. Energy Sustain Develop 2010;14:339–45.
[34] Karmakar A, Karmakar S, Souti Mukherjee S. Properties of various plants and animals feedstocks for biodiesel production. Bioresour Technol 2010;101:7201–10.
[35] Semwal S, Arora AK, Badoni RP, Tuli DK. Biodiesel production using heterogeneous catalysts: review. Bioresour Technol 2011;102:2151–61.
[36] Kenthorai RJ, Eng-Seng C, Ravindra P. Economic assessment of biodiesel production: comparison of alkali and biocatalyst processes. Renew Sustain Energy Rev 2011;15:745–51.
[37] Libuda J, Schauermann S, Laurin M, Schalow T, Freund HJ. Model studies in heterogeneous catalysis. From structure to kinetics. Monatshefte Chem/Chem Monthly 2005;136:59–76 [From the issue entitled “Applied Chemistry”].
[38] Hasheminejad M, Tabatabaei M, Mansourpanah Y, Khatami far M, Javani A. Upstream and downstream strategies to economize biodiesel production. Bioresour Technol 2011;102:461–8.
[39] Ebiura T, Echizen T, Ishikawa A, Kazuhito M, Baba T. Selective transesterification of triolein with methanol to methyl oleate and glycerol using alumina loaded with alkali metal salt as a solid-base catalyst. Appl Catal A: Gen 2005;283:111–6.
[40] Xie W, Hong P, Ligong C. Calcined Mg–Al hydrotalcites as solid base catalysts for methanolysis of soybean oil. J Mol Catal A: Chem 2006;246:24–32.
[41] Fabbri D, Bevoni V, Notari M, Rivetti F. Properties of a potential biofuel obtained from soybean oil by transmethylation with dimethyl carbonate. Fuel 2007;86:690–7.

[42] Wang L, Yang J. Transesterification of soybean oil with nano-MgO or not in supercritical and subcritical methanol. Fuel 2007;86:328–33.
[43] Arzamendi G, Campoa I, Arguinarena E, Sanchez M, Montes M, Gandia LM. Synthesis of biodiesel with heterogeneous NaOH/alumina catalysts: comparison with homogeneous NaOH. J Chem Eng 2007;134:123–30.
[44] Lopez DE, Bruce Jr DA, Lotero JGE. Transesterification of triacetin with methanol on solid acid and base catalysts. Appl Catal A: Gen 2005;295:97–105.
[45] Tateno T, Sasaki T. Process for producing fatty acid fuels comprising fatty acids esters. Uni. State Patent 6818026, November 16, 2004.
[46] Di Serio M, Tesser R, Dimiccoli M, Cammarota F, Nasatasi M, Santacesaria E. Synthesis of biodiesel via homogeneous Lewis acid catalysts. J Mol Catal 2005;239:111–5.
[47] Mootabadi H, Salamatinia B, Bhatia S, Abdullah AZ. Ultrasonic-assisted biodiesel production process from palm oil using alkaline earth metal oxides as the heterogeneous catalysts. Fuel 2010;89:1818–25.
[48] Salamatinia B, Mootabadi H, Bhatia S, Abdullah AZ. Optimization of ultrasonic-assisted heterogeneous biodiesel production from palm oil: a response surface methodology approach. Fuel Process Technol 2010;91:441–8.
[49] Vujicic DJ, Comic D, Zarubica A, Micic R, Boskovic G. Kinetics of biodiesel synthesis from sunflower oil over CaO heterogeneous catalyst. Fuel 2010;89:2054–61.
[50] Yoosuk B, Udomsap P, Buppa P, Pawnprapa K. Modification of calcite by hydration–dehydration method for heterogeneous biodiesel production process: the effects of water on properties and activity. J Chem Eng 2010;162:135–41.
[51] Yoo SJ, Lee HS, Bambang V, Kim J, Kim JD, Lee YW. Synthesis of biodiesel from rapeseed oil using supercritical methanol with metal oxide catalysts. Bioresour Technol 2010;101:8686–9.
[52] Sreeprasanth PS, Srivastava R, Srinivas D, Ratnasamy P. Hydrophobic, solid acid catalysts for production of biofuels and lubricants. Appl Catal A: Gen 2006;314:148–59.
[53] Yang Z, Xie W. Soybean oil transesterification over zinc oxide modified with alkali earth metals. Fuel Process Technol 2007;88:631–8.
[54] Garcia CM, Teixeira S, Marciniuk LL, Schuchardt U. Transesterification of soybean oil catalyzed by sulfated zirconia. Bioresour Technol 2008;99: 6608–13.
[55] Antunes WM, Veloso CO, Henriques CA. Transesterification of soybean oil with methanol catalyzed by basic solids. Catal Today 2008;133–135:548–54.
[56] Sun H, Ding Y, Duan J, Zhang Q, Wang Z, Lou H, et al. Transesterification of sunflower oil to biodiesel on ZrO_2 supported La_2O_3 catalyst. Bioresour Technol 2010;101:953–8.
[57] McNeff CV, McNeff LC, Yan B, Nowlan DT, Rasmussen M, Gyberg AE, et al. A continuous catalytic system for biodiesel production. Appl Catal A: Gen 2008;343:39–48.
[58] Xu L, Yang X, Yu X, Guo Y, Maynurkader. Preparation of mesoporous polyoxometalate–tantalum pentoxide composite catalyst for efficient esterification of fatty acid. Catal Commun 2008;9:1607–11.
[59] Hai-xin B, Xiao-Zhen S, Xiao-hua L, Shengyong L. Synthesis of porous CaO microsphere and its application in catalyzing transesterification reaction for biodiesel. Trans Nonferrous Met Soc China 2009;19:S674–7.
[60] Boz N, Degirmenbasi N, Kalyon DM. Conversion of biomass to fuel: transesterification of vegetable oil to biodiesel using KF loaded nano-g-Al_2O_3 as catalyst. Appl Catal B: Environ 2009;89:590–6.
[61] Yan S, Salley SO, Simon Ng KY. Simultaneous transesterification and esterification of unrefined or waste oils over ZnO–La_2O_3 catalysts. Appl Catal A: Gen 2009;353:203–12.
[62] Kansedo J, Lee KT, Bhatia S. Cerbera odollam (sea mango) oil as a promising non-edible feedstock for biodiesel production. Fuel 2009;88:1148–50.
[63] Liang X, Gong G, Wua H, Yang J. Highly efficient procedure for the synthesis of biodiesel from soybean oil using chloroaluminate ionic liquid as catalyst. Fuel 2009;88:613–6.
[64] Lukic I, Krstic J, Jovanovic D, Skala D. Alumina/silica supported K_2CO_3 as a catalyst for biodiesel synthesis from sunflower oil. Bioresour Technol 2009;100:4690–6.
[65] Noiroj K, Intarapong P, Luengnaruemitchai A, Jai-In S. A comparative study of KOH/Al_2O_3 and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. Renew Energy 2009;34:1145–50.
[66] Kumar S, Pulikottil AC, Sharma A, Sarkar M, Kagdiyal V, Yadav A, et al. A catalyst composition for transesterification of organically/naturally derived oils and fats to produce alkyl esters and process for preparing the same. WO 2010/020998:A2; 2010.
[67] Guo C, Baishan F. Preperation of solid acid catalyst from glucose – starch mixture for biodieselprouduction. Bioresour Technol 2011;102:2635–40.
[68] Ilgen O. Dolomite as a heterogeneous catalyst for transesterification of canola oil. Fuel Process Technol 2011;92:452–5.
[69] Furuta S, Matsuhashi H, Arata K. Biodiesel fuel production with solid amorphous-zirconia catalysis in fixed bed reactor. Biomass Bioenergy 2006;30:870–3.
[70] HolserRonald A, DollKenneth M, ErhanSevim Z. Metathesis of methyl soyate with ruthenium catalysts. Fuel 2006;85:393–5.
[71] Alsalme A, Kozhevnikova EF, Kozhevnikov IV. Heteropoly acids as catalysts for liquid-phase esterification and transesterification. Appl Catal A: Gen 2008;349:170–6.
[72] Jacobson K, Gopinath R, Meher LC, Dalai AK. Solid acid catalyzed biodiesel production from waste cooking oil. Appl Catal B: Environ 2008;85:86–91.
[73] Park YM, Lee Dw, Kim DK, Lee J, Lee KY. The heterogeneous catalyst system for the continuous conversion of free fatty acids in used vegetable oils for the production of biodiesel. Catal Today 2008;131:238–43.
[74] Park YM, Chung S, Eom HJ, Lee J, Lee K. Tungsten oxide zirconia as solid superacid catalyst for esterification of waste acid oil (dark oil). Bioresour Technol 2010;101:6589–93.
[75] Jackson MA, Mbaraka IK, Shanks BH. Esterification of oleic acid in supercritical carbon dioxide catalyzed by functionalized mesoporous silica and an immobilized lipase. Appl Catal A: Gen 2006;310:48–53.
[76] Liu Y, Lotero E, Goodwin Jr JG. Effect of carbon chain length on esterification of carboxylic acids with methanol using acid catalysis. J Catal 2006;243: 221–8.
[77] Liu R, Wang X, Zhao X, Feng P. Sulfonated ordered mesoporous carbon for catalytic preparation of biodiesel. Carbon 2008;46:1664–9.
[78] Perin G, Alvaro G, Westphal E, Viana LH, Jacob RG, Lenardao EJ, et al. Transesterification of castor oil assisted by microwave irradiation. Fuel 2008;87:2838–41.
[79] De Almeida Rusiene M, Noda Lucia K, Goncalves Norberto S, Meneghetti Simoni MP, Meneghetti Mario R. Transesterification reaction of vegetable oils, using superacid sulfated TiO_2–base catalysts. Appl Catal A: Gen 2008;347: 100–5.
[80] Melero JA, Vicente G, Morales G, Paniagua M, Moreno JM, Roldan R, et al. Acid-catalyzed etherification of bio-glycerol and isobutylene over sulfonic mesostructured silicas. Appl Catal A: Gen 2008;346:44–51.
[81] Juan JC, Zhang JC, Yarmo MA. Structure and reactivity of silica – supported zirconium sulfate for esterification of fatty acid under solvent – free condition. Appl Catal A: Gen 2007;332:209–15.
[82] Zhang J, Chen S, Yang R, Yan Y. Biodiesel production from vegetable oil using heterogeneous acid and alkali catalyst. Fuel 2010;89:2939–44.
[83] Zhu M, He B, Shi W, Yaohui FJD, Li J, Zeng F. Preparation and characterization of PSSA/PVA catalytic membrane for biodiesel production. Fuel 2010;89:2299–304.
[84] Alba-Rubio AC, Vila F, Alonso DM, Ojeda M, Mariscal R, Granados ML. Deactivation of organosulfonic acid functionalized silica catalysts during biodiesel synthesis. Appl Catal B: Environ 2010;95:279–87.
[85] Shu Q, Gao J, Nawaz Z, Liao Y, Wang D, Wang J. Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon based solid acid catalyst. Appl Energy 2010;87:2589–96.
[86] Baroutian S, Aroua MK, Abdul Raman AA, Nik Sulaiman NM. Potassium hydroxide catalyst supported on palm shell activated carbon for transesterification of palm oil. Fuel Process Technol 2010;91:1378–85.
[87] Dehkhoda AM, West AH, Ellis N. Biochar based solid acid catalyst for biodiesel production. Appl Catal A: Gen 2010;382:197–204.
[88] Deka DC, Basumatary S, Lee JS. High quality biodiesel from yellow oleander (*Thevetia peruviana*) seed oil. Biomass Bioenergy 2011;305:1797–803.
[89] Puna JF, Gomes JF, Correia MJ, Soares Dias AP, Bordado JC. Advances on the development of novel heterogeneous catalysts for transesterification of triglycerides in biodiesel. Fuel 2010;89:3602–6.
[90] Wei Z, Xu C, Li B. Application of waste eggshell as low-cost solid catalyst for biodiesel production. Bioresour Technol 2009;100:2883–5.
[91] Viriya-empikul N, Krasae P, Puttasawat B, Yoosuk B, Chollacoop N, Faungnawakij K. Waste shells of mollusk and egg as biodiesel production catalysts. Bioresour Technol 2010;101:3765–7.
[92] Chakraborty R, Bepari S, Banerjee A. Application of calcined waste fish (Labeo rohita) scale as low-cost heterogeneous catalyst for biodiesel synthesis. Bioresour Technol 2011;102:3610–8.
[93] Hama S, Yamaji H, Kaieda M, Oda M, Kondo A, Fukuda H. Effect of fatty acid membrane composition on whole-cell biocatalysts for biodiesel-fuel production. J Biochem Eng 2004;21:155–60.
[94] Oda M, Kaieda M, Hama S, Yamaji H, Kondo A, Izumoto E. Facilitatory effect of immobilized lipase-producing Rhizopus oryzae cells on acyl migration in biodiesel fuel production. J Biochem Eng 2004;23:45–51.
[95] Du W, Xu Y, Liu D, Zeng J. Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors. J Mol Catal B: Enzyme 2004;30:125–9.
[96] Alonso DM, Mariscal R, Moreno-Tost R, Poves MD, Granados M. Potassium leaching during triglyceride transesterification using K/γ-Al_2O_3 catalysts. Catal Commun 2007;8:2074–80.
[97] Barakos N, Pasias S, Papayannakos N. Transesterification of triglycerides in high and low quality oil feeds over an HT2 hydrotalcite catalyst. Bioresour Technol 2008;99:5037–42.
[98] Ngamcharussrivichai C, Totarat P, Bunyakiat K. Ca and Zn mixed oxide as a heterogeneous base catalyt for transterification of palm kernel oil. Appl Catal A: Gen 2008;341:77–85.
[99] Gao L, Teng G, Xiao G, Wei R. Biodiesel from palm oil via loading KF/Ca–Al hydrotalcite catalyst. Biomass Bioenergy 2010;34:1283–8.
[100] Narasimharao K, Mohapatra SK, Misra M. Quintinite as a bifunctional heterogeneous catalyst for biodiesel synthesis. Appl Catal A: Gen 2011;393:36–43.
[101] Di Serio M, Tesser R, Pengmei L, Santacesaria E. Heterogeneous catalysts for biodiesel production. Energy Fuels 2008;22:207–17.
[102] Veljkovic VB, Stamenkovic OS, Todorovic ZB, Lazic ML, Skala DU. Kinetics of sunflower oil methanolysis catalyzed by calcium oxide. Fuel 2009;88: 554–1562.
[103] Kouzu M, Kasuno T, Tajika M, Yamanaka S, Hidaka J. Active phase of calcium oxide used as solid base catalyst for transesterification of soybean oil with refluxing methanol. Appl Catal A: Gen 2008;334:357–65.

[104] Gryglewicz S. Rapeseed oil methyl esters preparation using heterogeneous catalysts. Bioresour Technol 1999;70:249–53.
[105] Kouzu M, Kasuno T, Tajika M, Sugimoto Y, Yamanaka S, Hidaka J. Calcium oxide as a solid base catalyst for transesterification of soybean oil and its application to biodiesel production. Fuel 2008;87:2798–806.
[106] Kawashima A, Matsubara K, Honda K. Acceleration of catalytic activity of calcium oxide for biodiesel production. Bioresour Technol 2009;100:696–700.
[107] Liu X, He H, wang Y, Zhu S. Transesterfication of soybean oil to biodiesel using SrO as a solid base catalyst. Catal Commun 2007;8:1107–11.
[108] Huaping ZHU, Zongbin WU, Yuanxiong C, Ping Z, Shijie D, Xiaohua L, et al. Preparation of biodiesel catalyzed by solid super base of calcium oxide and its refining process. J Chin Catal 2006;27:391–6.
[109] Taufiq-Yap YH, Lee HV, Hussein MZ, Yunus R. Calcium-based mixed oxide catalysts for methanolysis of Jatropha curcas oil to biodiesel. Biomass Bioenergy 2010;35:827–34.
[110] MacLeod Claire S, Harvey Adam P, Lee Adam F, Wilson Karen. Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. Chem Eng J 2008;135:63–70.
[111] Wen L, Wang Y, Lu D, Hu S, Han H. Preparation of KF/CaO nanocatalyst and its application in biodiesel production from Chinese tallow seed oil. Fuel 2010;89:2267–71.
[113] Dalai AKMG, Meher LC. Biodiesel productions from vegetable oils using heterogeneous catalysts and their applications as lubricity additives. In: IEEE EIC climate change technology conference. 2006 [EICCCC art 4057358].
[114] Encinar JM, Gonzalez JF, Pardal A, Martinez G. Rape oil transesterification over heterogeneous catalysts. Fuel Process Technol 2010;91:1530–6.
[115] Samart C, Chaiya C, Reubroycharoen P. Biodiesel production by methanolysis of soybean oil using calcium supported on mesoporous silica catalyst. Energy Convers Manage 2010;51:1428–31.
[116] Shumaker JL, Crofcheck C, Tackett SA, Santillan-Jimenez E, Morgan T, Ji Y, et al. Biodiesel synthesis using calcined layered double hydroxide catalysts. Appl Catal B: Environ 2008;82:120–30.
[117] Albuquerque CG, Santamara-Gonzalez J, Merida-Robles JM, Moreno-Tost R, Rodrıguez-Castellon E, Jimenez-Lopez A, et al. MgM (M = Al and Ca) oxides as basic catalysts in transesterification processes. Appl Catal A: Gen 2008;347:162–8.
[118] Zhang J, Chen S, Yang R, Yan Y. Biodiesel production from vegetable oil using heterogenous acid and alkali catalyst. Fuel 2010;89:2939–44.
[119] Toda M, Takagaki A, Okamura M, Kondo JN, Hayashi S, Domen K, et al. Green chemistry: biodiesel made with sugar catalyst. Nature 2005:178–438.
[120] Lou WY, Zong MH, Duan ZQ. Efficient production of biodiesel from high free fatty acid-containing waste oils using various carbohydrate-derived solid acid catalysts. Bioresour Technol 2008;99:8752–8.
[121] Faria EA, Ramalho HF, Marques JS, Suarez P, Prado A. Tetramethylguanidine covalently bonded onto silica gel surface as an efficient and reusable catalyst for transesterification of vegetable oil. Appl Catal A: Gen 2008;338: 72–8.
[122] Nakatani N, Takamori Takeda H, Sakugawa KH. Transesterification of soybean oil using combusted oyster shell waste as a catalyst. Bioresour Technol 2009;100:1510–3.
[123] Kondamudi N, Mohapatra SK, Misra M. Quintinite as a bifunctional heterogeneous catalyst for biodiesel synthesis. Appl Catal A: Gen 2011;393:36–43.
[124] Jitputti J, Kitiyanan B, Rangsunvigit P, Bunyakiat K, Attanatho L, Jenvanitpanjakul P. Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. J Chem Eng 2006;116:61–6.
[125] Xiao X, Tierney JW, Wender I. Alkylation of isobutene with 2-butene over anion modified zirconium oxide catalysts. Appl Catal A: Gen 1999;183:209–19.
[126] Stocker MN. Butane isomerization catalyzed by antimony pentafluride supported on sulfate-treated zirconium oxide. J Mol Catal 1985;29:371–7.
[127] Lopez DE, Suwannakarn K, Bruce DA, Goodwin Jr JG. Esterification and transesterification on tungstated zirconia: effect of calcination temperature. J Catal 2007;247:43–50.
[128] Da Silva RB, Lima Neto AF, dos Santos Lucas SS, de Oliveira Lima JR, Chaves MH, dos Santos Jr JR, et al. Catalysts of Cu(II) and Co(II) ions adsorbed in chitosan used in transesterification of soy bean and babassu oils – a new route for biodiesel syntheses. Bioresour Technol 2008;99:6793–8.
[129] Krohn BJ, McNeff CV, Yan B, Nowlan D. Production of algae-based biodiesel using the continuous catalytic Mcgyan process. Bioresour Technol 2011;102:94–100.
[130] Wang Y, Wu H, Zong MH. Improvement of biodiesel production by lipozyme TL IM-catalyzed methanolysis using response surface methodology and acyl migration enhancer. Bioresour Technol 2008;99:7232–7.
[131] Wen G, Yan Z, Smith M, Zhang P, Wen B. Kalsilite based heterogeneous catalyst for biodiesel production. Fuel 2010;89:2163–5.
[132] Yagiz F, Kazan D, Akin AN. Biodiesel production from waste oils by using lipase immobilized on hydrotalcite and zeolites. J Chem Eng 2007;134:262–7.
[133] Caetano CS, Fonseca IM, Ramos AM, Vital J, Castanheiro JE. Esterification of free fatty acids with methanol using heteropolyacids immobilized on silica. Catal Commun 2008;9:1996–9.
[134] MacLeod CS, Harvey AP, Lee AF, Wilson K. Evaluation of the activity and stability of alkali-doped metal oxide catalysts for application to an intensified method of biodiesel production. Chem Eng J 2008;135:63–70.
[135] Wimonrat T, Suriya P. Palm oil biodiesel synthesized with potassium loaded calcined hydrotalcite and effect of biodiesel blend on elastomer properties. Renew Energy 2008;33:1558–63.
[136] Zeng HY, Feng Z, Deng X, Li Y. Activation of Mg–Al hydrotalcite catalysts for transesterification of rape oil. Fuel 2008;87:3071–6.
[137] Guan G, Kusakabe K, Yamasaki S. Tri-potassium phosphate as a solid catalyst for biodiesel production from waste cooking oil. Fuel Process Technol 2009;90:520–4.
[138] Hameed BH, Lai LF, Chin LH. Production of biodiesel from palm oil (Elaeis guineensis) using heterogeneous catalyst: an optimized process. Fuel Process Technol 2009;90:606–10.
[139] Sree R, Babu NS, Prasad PSS, Lingaiah N. Transesterification of edible and non-edible oils over basic solid Mg/Zr catalysts. Fuel Process Technol 2009;90:152–7.
[140] Wen Z, Yu X, Tu ST, Yan J, Dahlquist E. Synthesis of biodiesel from vegetable oil with – methanol catalyzed by Li – doped magnesium oxide catalysts. Appl Energy 2010;87:743–8.
[141] Raita M, Champreda V, Laosiripojana N. Biocatalytic ethanolysis of palm oil for biodiesel production using microcrystalline lipase in tert-butanol system. Process Biochem 2010;45:829–34.
[142] Jiang W, Lu H, Qi T, Yan S, Liang B. Preparation, application, and optimization of Zn/Al complex oxides for biodiesel production under sub-critical conditions. Biotechnol Adv 2010;28:620–7.
[143] DaSilva RB, Lima Neto AF, Dos Santos LS, De Oliveira Lima JR, Chaves MH, Dos Santos Jr JR, et al. Catalysts of Cu(II) and Co(II) ions adsorbed in chitosan used in transesterification of soy bean and babassu oils – a new route for biodiesel syntheses. Bioresour Technol 1999;99:6793–8.
[144] Rashtizadeh E, Farzaneh F, Ghandi M. A comparative study of KOH loaded on double aluminosilicate layers, microporous and mesoporous materials as catalyst for biodiesel production via transesterification of soybean oil. Fuel 2010;89:3393–8.
[145] Yu X, Wen Z, Lin Y, Tu ST, Wang Z, Yan J. Intensification of biodiesel synthesis using metal foam reactors. Fuel 2010;89:3450–6.
[146] Georgogianni KG, Katsoulidis AP, Pomonis PJ, Kontominas MG. Transesterification of soybean frying oil to biodiesel using heterogeneous catalysts. Fuel Process Technol 2009;90:671–6.
[147] Glisic S, Lukic I, Skala D. Biodiesel synthesis at high pressure and temperature: analysis of energy consumption on industrial scale. Bioresour Technol 2009;100:6347–54.
[148] Suppes GJ, Dasari MA, Doskocil EJ, Mankidy PJ, Goff MJ. Transesterification of soybean oil with zeolite and metal catalysts. Appl Catal A: Gen 2004;257:213–23.
[149] Ramos MJ, Casas A, Rodriguez L, Romero R, Perez A. Transesterification of sunflower oil over zeolites using different metal loading: a case of leaching and agglomeration studies. Appl Catal A: Gen 2008;346:79–85.
[150] Chung KH, Chang DR, Park BG. Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts. Bioresour Technol 2008;99:7438–43.
[151] Suarez P, Plentz AZ, Meneghetti MSM, Wolf CR MR. Transformation of triglycerides into fuels, polymers and chemicals: some applications of catalysis in oleochemistry. Quim Nova 2007;30:667–76.
[152] Lotero E, Liu Y, Lopez DE, Suwannakarn K, Bruce DA, Goodwin Jr JG. Synthesis of biodiesel via acid catalysis. Ind Eng Chem Res 2005;44:5353–63.
[153] Muthu H, SathiyaSelvabala V, Varathachary TK, Selvaraj DK, Nandagopal J, Subramanian S. Synthesis of biodiesel from neem oil using sulfated zirconia via transesterification. J Braz Chem Eng 2010;27:601–8.
[154] Giri BY, Rao KN, Prabhavathi Devi BLA, Lingaiah N, Suryanarayana I, Prasad RBN, et al. Esterification of palmitic acid on the ammonium salt of 12-tungstophosphoric acid: the influence of partial proton exchange on the activity of the catalyst. Catal Commun 2005;6:788–92.
[155] Hamad B, de Souza L, Sapaly G, Rocha C, de Oliveira P, Gonzalez WA, et al. Transesterification of rapeseed oil with ethanol over heterogeneous heteropolyacids. Catal Commun 2008;10:92–7.
[156] Katada N, Hatanaka T, Ota M, Yamada K, Okumura K, Niwa M. Biodiesel production using heteropoly acid-derived solid acid catalyst $H_4PNb_bW_{11}O_{40}/WO_3–Nb_2O_5$. Appl Catal A: Gen 2009;363:164–8.
[157] Kolaczkowski ST, Asli UA, Davidson MG. A new heterogeneous ZnL_2 catalyst on a structured support for biodiesel production. Catal Today 2009;147S:S220–4.
[158] Li S, Wang Y, Dong S, Chen Y, Cao F. Biodiesel production from Eruca Sativa Gars vegetable oil and motor, emission properties. Renew Energy 2009;34:1871–6.
[159] Carmo Jr AC, De Souza Luiz KC, Da Costa Carlos EF, Longo E, Zamian JR, Da Rocha FGN. Production of biodiesel by esterification of palmitic acid over mesoporous aluminosilicate Al-MCM-41. Fuel 2009;88:461–8.
[160] Feng Y, He B, Cao B, Li J, Liu M, Yna F, et al. Biodiesel production using cation – exchange resin as heterogenous catalyst. Bioresour Technol 2010;101:1518–21.
[161] Cannilla C, Bonura G, Rombi E, Arenaa F, Frusteri F. Highly effective MnCeOx catalysts for biodiesel production by transesterification of vegetable oils with methanol. Appl Catal A: Gen 2010;382:158–66.
[162] Chen G, Fang B. Preperation of solid acid catalyst from glucose-starch mixture for biodiesel production. Bioresour Technol 2011;102:2635–40.
[163] Corro G, Tellez N, Ayala E, Marinez-Ayala A. Two-step biodiesel production from Jatropha curcas crude oil using SiO_2: HF solid catalyst for FFA esterification step. Fuel 2010;89:2815–21.
[164] Shi W, He B, Ding J, Li J, Yan F, Liang X. Preparation and characterization of the organic–inorganic hybrid membrane for biodiesel production. Bioresour Technol 2010;101:1501–5.

[165] Zhang S, Zu YG, Fu YJ, Luo M, Zhang DY, Efferth T. Rapid microwave-assisted transesterification of yellow horn oil to biodiesel using a heteropolyacid solid catalyst. Bioresour Technol 2010;101:931–6.

[166] Lin YC, Lee WJ, Hou HC. PAH emissions and energy efficiency of Palm-biodiesel blends fueled on diesel generator. Atmos Environ 2006;40:3930–40.

[167] Lin CY, Liun HA. Diesel engine performance and emission characteristics of biodiesel produced by the peroxidation process. Fuel 2006;85:298–305.

[168] Lin VSY, Radu DR. Use of functionalized mesoporous silicates to esterify fatty acids and transesterify oils. Unit. State Patent 7,122-688 B2; 2006.

[169] Macario A, Giordano G, Onida B, Cocina D, Tagarelli A, Giuffre AM. Biodiesel production process by homogeneous/heterogeneous catalystic system using an acid–base catalyst. Appl Catal A: Gen 2010;378:160–8.

[170] Nassreddine S, Karout A, Christ ML, Pierre AC. Transesterification of a vegetal oil with methanol catalyzed by a silica fibre reinforced aerogel encapsulated lipase. Appl Catal A: Gen 2008;344:70–7.

[171] Suwannakarn K, Lotero E, Changqing Lu S J.G. Jr. Stability of sulfated zirconia and the nature of the catalytically active species in the transesterification of triglycerides. J Catal 2008;255:279–86.

[172] Wang Y, Zhang F, Xu S, Yang L, Li D, Evans DG, et al. Preparation of macrospherical magnesia-rich magnesium aluminate spinel catalysts for methanolysis of soybean oil. Chem Eng Sci 2008;63:4306–12.

[173] Xi Y, Davis RJ. Influence of water on the activity and stability of activated Mg–Al hydrotalcites for the transesterification of tributyrin with methanol. J Catal 2008;254:190–7.

[174] Brun N, Garcia AB, Deleuze H, Achard MF, Sanchez C, Durand F, et al. Enzyme-based hybrid macroporous foams as highly efficient biocatalysts obtained through integrative chemistry. Chem Mater 2010;22: 4555–62.

[175] Winayanuwattikun P, Kaewpiboon C, Piriyakananon K, Tantong S, Thakernkarnkit W, Chulalaksananukul W, et al. Potential plant oil feedstock for lipase-catalyzed biodiesel production in Thailand. Biomass Bioenergy 2008; 32:1279–86.

[176] Park EY, Sato S M., Kojima S S. Lipase-catalyzed biodiesel production from waste activated bleaching earth as raw material in a pilot plant. Bioresour Technol 2008;99:3130–5.